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Coated Detergent Tablets

This invention relates generally to compact shaped bodies having detersive properties. Such detersive shaped bodies include, for example, laundry detergent tablets, tablets for dishwashing machines or for cleaning hard surfaces, bleach tablets for use in washing or dishwashing machines, water softening tablets or stain remover tablets. More particularly, the present invention relates to laundry detergent tablets which are used for washing laundry in domestic washing machines and which are referred to in short as detergent tablets.

Detergent tablets are widely described in the prior-art literature and are enjoying increasing popularity among consumers because they are easy to dose. Tabletted detergents have a number of advantages over powder-form detergents: they are easier to dose and handle and, by virtue of their compact structure, have advantages in regard to storage and transportation. As a result, detergent shaped bodies are also comprehensively described in the patent literature. One problem which repeatedly arises in the use of detergent tablets is the inadequate disintegrating and dissolving rate of the tablets under in-use conditions. Since sufficiently stable, i.e. dimensionally stable and fracture-resistant, tablets can only be produced by applying relatively high pressures, the ingredients of the tablet are heavily compacted so that disintegration of the tablet in the wash liquor is delayed which results in excessively slow release of the active substances in the washing process. The delayed disintegration of the tablets has the further disadvantage that typical detergent tablets cannot be flushed into the washing process from the dispensing compartment of domestic washing machines because the tablets do not disintegrate sufficiently quickly into secondary particles which

are small enough to be flushed from the dispensing compartment into the drum of the washing machine. Another problem which occurs with detergent tablets in particular lies in the friability of the tablets and their often inadequate resistance to abrasion. Thus, although sufficiently fracture-resistant, i.e. hard, detergent tablets can be produced, they are often not strong enough to withstand the loads encountered during packaging, transportation and handling, i.e. impact and friction effects, so that broken edges and signs of abrasion spoil the appearance of the tablet or even lead to the complete destruction of its structure.

Many solutions have been developed in the prior art to overcome the dichotomy between hardness, i.e. transportation and handling stability, and easy disintegration of the tablets. One solution known in particular from the field of pharmacy and extended to detergent tablets is to incorporate certain disintegration aids which facilitate the access of water and which swell on contact with water and effervesce or otherwise disintegrate. Other solutions proposed in the patent literature are based on the compression of premixes of certain particle sizes, the separation of individual ingredients from certain other ingredients and the coating of individual ingredients or the entire tablet with binders.

The coating of detergent tablets is the subject of certain patent applications.

Thus, European patent applications **EP 846 754, EP 846 755** and **EP 846 756** (Procter & Gamble) describe coated detergent tablets comprising a "core" of compacted particulate detergent and a coating, dicarboxylic acids, more particularly adipic acid, optionally containing other ingredients, for example disintegration aids, being used as the coating materials.

Coated detergent tablets are also the subject of European patent application **EP 716 144** (Unilever). According to the disclosure of this document, the hardness of the tablets can be increased by a coating

without any adverse effect on the tablet disintegration and dissolving times. Film-forming substances, more particularly copolymers of acrylic acid and maleic acid or sugars, are mentioned as coating materials.

The documents cited above contain little information on the application of the coating. They also provide no particulars of the coating thickness.

Whereas, according to the teaching of the first of the documents cited above, far more than 5% by weight of the total weight of the coated tablet consists of coating material, the figure is still at least 1% by weight according to the teaching of the last of the cited documents. In addition, the solutions proposed in the prior art also require individual wrapping of the tablets. To this end, the tablets have to be wrapped in film as individual tablets or as dosage units which may consist, for example, of two tablets to ensure than the tablets retain their hardness and their fast disintegration times in storage. Only after this individual wrapping of tablets can the pack as a whole as supplied to the consumer be boxed.

Now, the problem addressed by the present invention was to provide coated detergent tablets where the advantageous properties of relatively high hardness values compared with short disintegration times would be achieved with smaller quantities of coating materials, at most 1% by weight and, preferably, significantly less of the tablet as a whole being made up by the coating material. In particular, the resistance of the tablets to impact and friction would be further improved in relation to known tablets despite a distinct reduction in the amount of coating material used. Ideally, the coated tablets would be able to be supplied to the consumer with minimized packaging, i.e. in more cost efficient individual packs or even without such packs, without any adverse effect on the storage stability of the tablets. Another problem addressed by the present invention was to provide a simple and universally usable process for the production of such coated tablets.

It has now been found that certain water-soluble polymers are suitable for coating detergent tablets, even in extremely small quantities, and provide them with advantageous properties.

Accordingly, the present invention relates to detergent tablets of compacted particulate detergent containing builder(s), surfactant(s) and optionally other detergent ingredients which are coated with a polymer or polymer mixture, the polymer or at least 50% by weight of the polymer mixture being selected from

a) water-soluble nonionic polymers from the group of
- a1) polyvinyl pyrrolidones,
- a2) vinyl pyrrolidone/vinyl ester copolymers,
- a3) cellulose ethers

b) water-soluble amphoteric polymers from the group of
- b1) alkyl acrylamide/acrylic acid copolymers,
- b2) alkyl acrylamide/methacrylic acid copolymers,
- b3) alkyl acrylamide/methyl methacrylic acid copolymers,
- b4) alkyl acrylamide/acrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,
- b5) alkyl acrylamide/methacrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,
- b6) alkyl acrylamide/methyl methacrylic acid/alkylaminoalkyl (meth)-acrylic acid copolymers,
- b7) alkyl acrylamide/alkyl methacrylate/alkylaminoethyl methacrylate/ alkyl methacrylate copolymers,
- b8) copolymers of
  - b8i) unsaturated carboxylic acids,
  - b8ii) cationically derivatized unsaturated carboxylic acids,
  - b8iii) optionally other ionic or nonionic monomers,

c) water-soluble zwitterionic polymers from the group of

c1) acrylamidoalkyl trialkylammonium chloride/acrylic acid copolymers and alkali metal and ammonium salts thereof,

c2) acrylamidoalkyl trialkylammonium chloride/methacrylic acid copolymers and alkali metal and ammonium salts thereof,

c3) methacroyl ethyl betaine/methacrylate copolymers,

d) water-soluble anionic polymers from the group of

d1) vinyl acetate/crotonic acid copolymers,

d2) vinyl pyrrolidone/vinyl acrylate copolymers,

d3) acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,

d4) graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or polyalkylene glycols,

d5) grafted and crosslinked copolymers from the copolymerization of

- d5i) at least one monomer of the nonionic type,
- d5ii) at least one monomer of the ionic type,
- d5iii) polyethylene glycol and
- d5iv) a crosslinking agent,

d6) copolymers obtained by copolymerization of at least one monomer of each of the following three groups:

- d6i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,
- d6ii) unsaturated carboxylic acids,
- d6iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group d6ii) with saturated or unsaturated, linear or branched C_{8-18} alcohols,

d7) terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl ester,

d8) tetrapolymers and pentapolymers of

d8i) crotonic acid or allyloxyacetic acid,

d8ii) vinyl acetate or vinyl propionate,

d8iii) branched allyl or methallyl esters,

d8iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters,

d9) crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinyl benzene, vinyl methyl ether, acrylamide and water-soluble salts thereof,

d10) terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic monocarboxylic acid branched in the α-position,

e) water-soluble cationic polymers from the group of

e1) quaternized cellulose derivatives,

e2) polysiloxanes containing quaternary groups,

e3) cationic guar derivatives,

e4) polymeric dimethyl diallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid,

e5) copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate,

e6) vinyl pyrrolidone/methoimidazolinium chloride copolymers,

e7) quaternized polyvinyl alcohol,

e8) polymers known by the INCI names of polyquaternium 2, polyquaternium 17, polyquaternium 18 and polyquaternium 27.

Water-soluble polymers in the context of the invention are polymers of which more than 2.5% by weight are soluble in water at room temperature.

The detergent tablets according to the invention are coated with a polymer or polymer mixture, the polymer (and hence the entire coating) or at least 50% by weight of the polymer mixture (and hence at least 50% of the coating) being selected from certain polymers. In this case, all the coating or at least 50% of its weight consists of water-soluble polymers from the group of nonionic, amphoteric, zwitterionic, anionic and/or cationic polymers. These polymers are described in more detail in the following.

According to the invention, preferred water-soluble polymers are nonionic. The following are examples of suitable nonionic polymers:

- Polyvinyl pyrrolidones which are marketed, for example, under the name of Luviskol® (BASF). Polyvinyl pyrrolidones are preferred nonionic polymers for the purposes of the invention.

  Polyvinyl pyrrolidones [poly(1-vinyl-2-pyrrolidinones)], PVPs for short, are polymers corresponding to general formula (I):

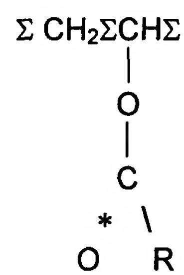
  (I)

  which are obtained by radical polymerization of 1-vinyl pyrrolidone by solution or suspension polymerization using radical formers (peroxides, azo compounds) as initiators. The ionic polymerization of the monomer only gives products of low molecular weight. Commercially available polyvinyl pyrrolidones have molecular weights of about 2500 to 750,000 g/mole which are characterized by expressing the K values and - depending on their K value - have glass transition temperatures of 130 to 175°C. They are marketed as white hygroscopic powders or as

aqueous solutions. Polyvinyl pyrrolidones are readily soluble in water and in a number of organic solvents (alcohols, ketones, glacial acetic acid, chlorinated hydrocarbons, phenols, etc.).

Σ Vinyl pyrrolidone/vinyl acetate copolymers which are marketed, for example under the registered name of Luviskol® (BASF). Luviskol® VA 64 and Luviskol® VA 73, both vinyl pyrrolidone/vinyl acetate copolymers, are particularly preferred nonionic polymers.

The vinyl ester polymers are polymers obtainable from vinyl esters containing a group corresponding to formula (II):



(II)

as the characteristic basic unit of the macromolecules. Of these, the vinyl acetate polymers (R = CH_3) with polyvinyl acetates, as by far the most important representatives, have the greatest commercial significance. The polymerization of the vinyl esters is carried out by various radical polymerization processes (solution polymerization, suspension polymerization, emulsion polymerization, bulk polymerization). Copolymers of vinyl acetate with vinyl pyrrolidone contain monomer units corresponding to formulae (I) and (II).

Σ Cellulose ethers, such as hydroxypropyl cellulose, hydroxyethyl cellulose and methyl hydroxypropyl cellulose, which are marketed for example under the registered names of Culminal® and Benecel® (AQUALON).

Cellulose ethers correspond to general formula (III):

(III)

in which R represents H or an alkyl, alkenyl, alkinyl, aryl or alkylaryl group. In preferred products, at least one R in formula (III) stands for $-CH_2CH_2CH_2$-OH or -CH_2CH_2-OH. On an industrial scale, cellulose ethers are produced by etherification of alkali metal cellulose (for example with ethylene oxide). Cellulose ethers are characterized by the average degree of substitution DS or the molar degree of substitution MS which indicate how many hydroxy groups of an anhydroglucose unit of the cellulose have reacted with the etherifying agent or how many moles of the etherifying agent on average have been added onto one anhydroglucose unit. Hydroxyethyl celluloses are soluble in water where they have a DS of about 0.6 or higher or an MS of about 1 or higher. Commercially available hydroxyethyl or hydroxypropyl celluloses have degrees of substitution of 0.85 to 1.35 (DS) or 1.5 to 3 (MS). Hydroxyethyl and hydroxypropyl celluloses are marketed as yellowish-white, odorless and tasteless powders with various degrees of polymerization. Hydroxyethyl and hydroxypropyl celluloses are soluble in cold and hot water and in certain (water-containing) organic solvents, but are insoluble in most (water-free) organic solvents. Their aqueous solutions are relatively non-sensitive to changes in pH or to the addition of an electrolyte.

Other polymers suitable for the purposes of the invention are water-soluble "amphopolymers". "Amphopolymers" is the generic term for amphoteric polymers, i.e. polymers which contain both free amino groups

and free -COOH or -SO_3H groups in the molecule and which are capable of forming inner salts, zwitterionic polymers which contain quaternary ammonium groups and -$COO^{\ominus}$ or -$SO_3^{\ominus}$ groups in the molecule, and for polymers which contain -COOH or -SO_3H groups and quaternary ammonium groups. One example of an amphopolymer suitable for use in accordance with the invention is the acrylic resin obtainable under the name of Amphomer®, which is a copolymer of tert.butyl aminoethyl methacrylate, N-(1,1,3,3-tetramethylbutyl)acrylamide and two or more monomers from the group consisting of acrylic acid, methacrylic acid and simple esters thereof. Other preferred amphopolymers consist of unsaturated carboxylic acids (for example acrylic and methacrylic acid), cationically derivatized unsaturated carboxylic acids (for example acrylamidopropyl trimethyl ammonium chloride) and optionally other ionic or nonionic monomers as known, for example, from **DE-A-39 29 973** and the prior art literature cited therein. According to the invention, terpolymers of acrylic acid, methyl acrylate and methacrylamidopropyl trimonium chloride, which are commercially available under the name of Merquat® 2001 N, are particularly preferred amphopolymers. Other suitable amphoteric polymers are, for example, the octyl acrylamide/methyl methacrylate/tert.butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers obtainable under the names of Amphomer® and Amphomer® LV-71 (DELFT NATIONAL).

Suitable zwitterionic polymers are, for example, the polymers disclosed in German patent applications **DE 39 29 973, DE 21 50 557, DE 28 17 369** and **DE 37 08 451**. Acrylamidopropyl trimethylammonium chloride/acrylic acid or methacrylic acid copolymers and alkali metal and ammonium salts thereof are preferred zwitterionic polymers. Other suitable zwitterionic polymers are methacroyl ethyl betaine/methacrylate copolymers which are commercially obtainable under the name of Amersette® (AMERCHOL).

Anionic polymers suitable for the purposes of the present invention include:

Σ Vinyl acetate/crotonic acid copolymers which are marketed, for example, under the names of Resyn® (NATIONAL STARCH), Luviset® (BASF) and Gafset® (GAF).
Besides monomer units corresponding to formula (II) above, these polymers also contain monomer units corresponding to general formula (IV):

$$[\text{-CH(CH}_3\text{)-CH(COOH)-}]_n \qquad \text{(IV)}$$

Σ Vinyl pyrrolidone/vinyl acrylate copolymers obtainable, for example, under the registered name of Luviflex® (BASF). A preferred polymer is the vinyl pyrrolidone/acrylate terpolymer obtainable under the name of Luviflex® VBM-35 (BASF).

Σ Acrylic acid/ethylacrylate/N-tert.butyl acrylamide terpolymers which are marketed, for example, under the name of Ultrahold® strong (BASF).

Σ Graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or polyalkylene glycols.
Corresponding grafted polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture with other copolymerizable compounds on polyalkylene glycols are obtained by high-temperature polymerization in homogeneous phase by stirring the polyalkylene glycols into the monomers, i.e. vinyl esters, esters of acrylic or methacrylic acid, in the presence of radical formers.

Suitable vinyl esters are, for example, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate while suitable esters of acrylic or methacrylic acid are those obtainable with low molecular weight aliphatic alcohols, i.e. in particular ethanol, propanol, isopropanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2,2-dimethyl-1-propanol, 3-methyl-1-butanol; 3-methyl-2-butanol, 2-methyl-2-butanol, 2-methyl-1-butanol, 1-hexanol. Suitable polyalkylene glycols are, in particular, polyethylene glycols and polypropylene glycols. Polymers of ethylene glycol which correspond to general formula (V):

$$H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH \qquad (V)$$

where n may assume values of 1 (ethylene glycol) to several thousand. Various nomenclatures are used for polyethylene glycols which can lead to confusion. It is common practice to indicate the mean relative molecular weight after the initials "PEG", so that "PEG 200" characterizes a polyethylene glycol having a relative molecular weight of about 190 to about 210. Cosmetic ingredients are covered by another nomenclature in which the initials PEG are followed by a hyphen and the hyphen is in turn directly followed by a number which corresponds to the index n in general formula V above. Under this nomenclature (so-called INCI nomenclature, **CTFA International Cosmetic Ingredient Dictionary and Handbook, 5th Edition,** The Cosmetic, Toiletry and Fragrance Association, Washington, 1997), PEG-4, PEG-6, PEG-8, PEG-9, PEG-10, PEG-12, PEG-14 and PEG-16, for example, may be used. Polyethylene glycols are commercially obtainable, for example, under the names of Carbowax® PEG 200 (Union Carbide), Emkapol® 200 (ICI Americas), Lipoxol® 200 MED (HÜLS America), Polyglycol® E-200 (Dow Chemical), Alkapol® PEG

300 (Rhone-Poulenc), Lutrol® E300 (BASF) and the corresponding commercial names with higher numbers.

Polypropylene glycols (PPGs) are polymers of propylene glycol which correspond to general formula (VI):

$$H\text{-}(O\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2)_n\text{-}OH \qquad \text{(VI)}$$

where n may assume a value of 1 (propylene glycol) to several thousand. Di-, tri- and tetrapropylene glycol, i.e. representatives where n = 2, 3 and 4 in formula VI, are of particular commercial significance.

More particularly, the vinyl acetate copolymers grafted onto polyethylene glycols and the polymers of vinyl acetate and crotonic acid grafted onto polyethylene glycols may be used.

Σ Grafted and crosslinked copolymers from the copolymerization of

i) at least one monomer of the nonionic type,

ii) at least one monomer of the ionic type,

iii) polyethylene glycol and

iv) a crosslinking agent.

The polyethylene glycol used has a molecular weight of 200 to several million and preferably in the range from 300 to 30,000.

The nonionic monomers may be of various types, among which the following are preferred: vinyl acetate, vinyl stearate, vinyl laurate, vinyl propionate, allyl stearate, allyl laurate, diethyl maleate, allyl acetate, methyl methacrylate, cetyl vinyl ether, stearyl vinyl ether and 1-hexene.

The nonionic monomers may also be of various types, among which crotonic acid, allyloxyacetic acid, vinyl acetic acid, maleic acid, acrylic acid and methacrylic acid are present with particular advantage in the graft polymers.

Preferred crosslinking agents are ethylene glycol dimethacrylate, diallyl phthalate, ortho-, meta- and para-divinyl benzene, tetraallyloxy ethane and polyallyl saccharoses containing 2 to 5 allyl groups per molecule of saccharin.

The grafted and crosslinked copolymers described above are preferably formed from:

i) 5 to 85% by weight of at least one monomer of the nonionic type,

ii) 3 to 80% by weight of at least one monomer of the ionic type,

iii) 2 to 50% by weight and preferably 5 to 30% by weight of polyethylene glycol and

iv) 0.1 to 8% by weight of a crosslinking agent, the percentage of the crosslinking agent being determined by the ratio of the total weights of i), ii) and iii).

Σ Copolymers obtained by copolymerization of at least one monomer of each of the following three groups:

i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,

ii) unsaturated carboxylic acids,

iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group ii) with saturated or unsaturated, linear or branched C_{8-18} alcohol.

Short-chain carboxylic acids or alcohols in the context of the present invention are understood to be those containing 1 to 8 carbon atoms, the carbon chains of these compounds optionally being interrupted by two-bond hetero groups, such as -O-, -NH-, -S-.

Σ Terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl ester.

These terpolymers contain monomer units corresponding to general formulae (II) and (IV) (see above) and monomer units of one or more allyl or methallyl esters corresponding to formula (VII):

$$R^2\text{-}\overset{\displaystyle R^1}{\underset{\displaystyle CH_3}{C}}\text{-}C(O)\text{-}O\text{-}CH_2X\overset{\displaystyle R^3}{C}{=}CH_2 \qquad \text{(VII)}$$

where R^3 represents -H or $-CH_3$, R^2 represents $-CH_3$ or $-CH(CH_3)_2$ and R^1 represents $-CH_3$ or is a saturated, linear or branched C_{1-6} alkyl group and the sum of the carbon atoms in the substituents R^1 and R^2 is preferably 7, 6, 5, 4, 3 or 2.

The terpolymers mentioned above preferably result from the copolymerization of 7 to 12% by weight of crotonic acid, 65 to 86% by weight and preferably 71 to 83% by weight of vinyl acetate and 8 to 20% by weight and preferably 10 to 17% by weight of allyl or methallyl esters corresponding to formula (VII).

Σ Tetrapolymers and pentapolymers of

i) crotonic acid or allyloxyacetic acid,

ii) vinyl acetate or vinyl propionate,

iii) branched allyl or methallyl esters,

iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters.

Σ Crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinyl benzene, vinyl methyl ether, acrylamide and water-soluble salts thereof.

Σ Terpolymers of vinyl acetate, crotonic acid and vinyl esters of a

saturated aliphatic monocarboxylic acid branched in the α-position.

Other polymers usable with advantage as part of the coating are cationic polymers. Among the cationic polymers, permanently cationic polymers are preferred. In the context of the invention, "permanently cationic" polymers are polymers which contain a cationic group irrespective of the pH value of the detergent (i.e. both the coating and the tablet). Such polymers are generally polymers which contain a quaternary nitrogen atom, for example in the form of an ammonium group.

The following are examples of preferred cationic polymers:

Σ Quaternized cellulose derivatives commercially obtainable under the names of Celquat® and Polymer JR®. The compounds Celquat® H 100, Celquat® L 200 and Polymer JR® 400 are preferred quaternized cellulose derivatives.

Σ Polysiloxanes containing quaternary groups such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silylamodimethicone), Dow Corning® 929 Emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, quaternium-80).

Σ Cationic guar derivatives such as, in particular, the products marketed under the names of Cosmedia®Guar and Jaguar®.

Σ Polymeric dimethyl diallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid. The products commercially obtainable under the names of Merquat® 100

(poly(dimethyl diallylammonium chloride)) and Merquat® 550 (dimethyl diallylammonium chloride/acrylamide copolymer) are examples of such cationic polymers.

- Σ Copolymers of vinyl pyrrolidone with quaternized derivatives of dialkyl aminoacrylate and methacrylate, such as for example vinyl pyrrolidone/ dimethylaminomethacrylate copolymers quaternized with diethyl sulfate. Compounds such as these are commercially available under the names of Gafquat® 734 and Gafquat® 755.

- Σ Vinyl pyrrolidone/methoimidazolinium chloride copolymers as marketed under the name of Luviquat®.

- Σ Quaternized polyvinyl alcohol

and the polymers containing quaternary nitrogen atoms in the main polymer chain known by the names of

- Σ polyquaternium 2,
- Σ polyquaternium 17,
- Σ polyquaternium 18 and
- Σ polyquaternium 27.

The names of the above-mentioned polymers are based on the so-called INCI nomenclature: particulars can be found in the CTFA International Cosmetic Ingredient Dictionary and Handbook, 5th Edition, The Cosmetic, Toiletry and Fragrance Association, Washington, 1997, to which reference is expressly made here.

According to the invention, preferred cationic polymers are quaternized cellulose derivatives and polymeric dimethyl diallylammonium salts and copolymers thereof. Cationic cellulose derivatives, more

particularly the commercial product Polymer® JR 400, are most particularly preferred cationic polymers.

The detergent tablets coated in accordance with the invention have distinctly improved properties even with small amounts of coating material. In a preferred embodiment of the invention, the quantity of coating material makes up less than 1% by weight, preferably less than 0.5% by weight and more preferably less than 0.25% by weight of the total weight of the coated tablet. Accordingly, detergent tablets where the ratio by weight of uncoated tablet to coating is greater than 100:1, preferably greater than 250:1 and more preferably greater than 500:1 are preferred embodiments of the present invention.

By virtue of the small quantities in which the polymers mentioned above form a high-strength and advantageous coating around the pre-compressed detergent tablets, it is possible to achieve coating thicknesses which are small by comparison with the dimensions of the tablets. In preferred detergent tablets, the thickness of the coating on the tablet is between 0.1 and 150 µm, preferably between 0.5 and 100 µm and more preferably between 5 and 50 µm.

In order to make the coating even more resistant to mechanical stressing, polyurethanes may be incorporated therein. Polyurethanes provide the coating with elasticity and stability and, after the above-mentioned quantity of water-soluble polymer, may make up as much as 50% by weight of the coating.

In the context of the present invention, polyurethanes are insoluble in water if less than 2.5% by weight dissolves in water at room temperature.

The polyurethanes consist of at least two different types of monomer, namely:

- a compound (A) containing at least 2 active hydrogen atoms per molecule and
- a diisocyanate or polyisocyanate (B).

The compounds (A) may be, for example, diols, triols, diamines, triamines, polyetherols and polyesterols. The compounds containing more than 2 active hydrogen atoms are normally used in only small quantities in combination with a large excess of compounds containing 2 active hydrogen atoms.

Examples of compounds (A) are ethylene glycol, 1,2- and 1,3-propylene glycol, butylene glycols, di-, tri-, tetra- and poly-ethylene and -propylene glycols, copolymers of lower alkylene oxides, such as ethylene oxide, propylene oxide and butylene oxide, ethylenediamine, propylenediamine, 1,4-diaminobutane, hexamethylenediamine and α,ω-diamines based on long-chain alkanes or polyalkylene oxides.

According to the invention, polyurethanes in which the compounds (A) are diols, triols and polyetherols can be preferred. In some cases, polyethylene glycols and polypropylene glycols in particular with molecular weights in the range from 200 to 3000 and more particularly in the range from 1600 to 2500 have proved to be particularly suitable. Polyesterols are normally obtained by modifying the compound (A) with dicarboxylic acids, such as phthalic acid, isophthalic acid and adipic acid.

The compounds (B) used are mainly hexamethylene diisocyanate, 2,4- and 2,6-toluene diisocyanate, 4,4'-methylene di(phenylisocyanate) and, more particularly, isophorone diisocyanate. These compounds may be described by the following general formula:

$$O{=}C{=}N\text{-}R^4\text{-}N{=}C{=}O \qquad \text{(VIII)}$$

in which R^4 is a connecting group of carbon atoms, for example a methylene, ethylene, propylene, butylene, pentylene, hexylene etc. group. In the above-mentioned and, industrially, most widely used hexamethylene diisocyanate (HMDI), R^4 = $(CH_2)_6$; in 2,4- and 2,6-toluene diisocyanate (TDI), R^4 = C_6H_3-CH_3); in 4,4'-methylene di(phenylisocyanate) (MDI), R^4 =

C_6H_4-CH_2-C_6H_4 and, in isophorone diisocyanate, R^4 = the isophorone residue (3,5,5-trimethyl-2-cyclohexenone).

In addition, the polyurethanes used in accordance with the invention may contain such structural units as, for example, diamines as chain extenders and hydroxycarboxylic acids. Dialkylol carboxylic acids such as, for example, dimethylol propionic acid are particularly suitable hydroxycarboxylic acids. So far as the other structural units are concerned, it makes no difference in principle whether they are nonionic, anionic or cationic.

Further information on the structure and production of the polyurethanes can be found in the articles in the relevant reference books, such as **Römpps Chemie-Lexikon** and **Ullmanns Enzyklopädie der technischen Chemie**.

In many cases, polyurethanes which may be characterized as follows have proved to be particularly suitable for the purposes of the present invention:

- solely aliphatic groups in the molecule,
- no free isocyanate groups in the molecule,
- polyether and polyester polyurethanes,
- anionic groups in the molecule.

In addition, it has proved to be of advantage so far as the production of the coated detergent tablets according to the invention is concerned if the polyurethanes are not directly mixed with the other components, but instead are introduced in the form of aqueous dispersions. Such dispersions normally have a solids content of about 20 to 50% and, more particularly, about 35 to 45% and are also commercially obtainable.

According to the invention, detergent tablets of which the coating contains polyurethanes in quantities of 5 to 50% by weight, preferably 7.5 to 40% by weight and more preferably 10 to 30% by weight, based on the coating, in addition to the polymers mentioned are preferred.

The constituents of the coating of the tablets according to the

invention are described in detail in the foregoing. The constituents of the tablets per se, i.e. the uncoated tablets, are described in the following. These tablets are referred to hereinafter partly as "basic tablets" in order to make a verbal distinction from the term "tablet" for the detergent tablets coated in accordance with the invention and partly by the general term "tablet". Since the subject of the present invention are basic tablets provided with a coating, the observations made in the following in reference to the basic tablet naturally apply equally to detergent tablets according to the invention which satisfy the corresponding requirements and vice versa.

The basic tablets contain builder(s) and surfactant(s) as essential ingredients. The basic tablets according to the invention may contain any of the builders typically used in detergents, i.e. in particular zeolites, silicates, carbonates, organic co-builders and also - providing there are no ecological objections to their use - the phosphates.

Suitable crystalline layer-form sodium silicates correspond to the general formula $NaMSi_xO_{2x+1}A$ y H_2O, where M is sodium or hydrogen, x is a number of 1.9 to 4 and y is a number of 0 to 20, preferred values for x being 2, 3 or 4. Crystalline layer silicates such as these are described, for example, in European patent application **EP-A-0 164 514**. Preferred crystalline layer silicates corresponding to the above formula are those in which M is sodium and x assumes the value 2 or 3. Both β- and δ-sodium disilicates $Na_2Si_2O_5A$ y H_2O are particularly preferred, β-sodium disilicate being obtainable, for example, by the process described in International patent application **WO-A- 91/08171**.

Other useful builders are amorphous sodium silicates with a modulus ($Na_2O:SiO_2$ ratio) of 1:2 to 1:3.3, preferably 1:2 to 1:2.8 and more preferably 1:2 to 1:2.6 which dissolve with delay and exhibit multiple wash cycle properties. The delay in dissolution in relation to conventional amorphous sodium silicates can have been obtained in various ways, for example by surface treatment, compounding, compacting or by overdrying.

In the context of the invention, the term Aamorphous≅ is also understood to encompass AX-ray amorphous≅. In other words, the silicates do not produce any of the sharp X-ray reflexes typical of crystalline substances in X-ray diffraction experiments, but at best one or more maxima of the scattered X-radiation which have a width of several degrees of the diffraction angle. However, particularly good builder properties may even be achieved where the silicate particles produce crooked or even sharp diffraction maxima in electron diffraction experiments. This may be interpreted to mean that the products have microcrystalline regions between 10 and a few hundred nm in size, values of up to at most 50 nm and, more particularly, up to at most 20 nm being preferred. So-called X-ray amorphous silicates such as these, which also dissolve with delay in relation to conventional waterglasses, are described for example in German patent application **DE-A-44 00 024**. Compacted amorphous silicates, compounded amorphous silicates and overdried X-ray-amorphous silicates are particularly preferred.

The finely crystalline, synthetic zeolite containing bound water used in accordance with the invention is preferably zeolite A and/or zeolite P. Zeolite MAP® (Crosfield) is a particularly preferred P-type zeolite. However, zeolite X and mixtures of A, X and/or P are also suitable. According to the invention, it is also preferred to use, for example, a co-crystallizate of zeolite X and zeolite A (ca. 80% by weight zeolite X) which is marketed by CONDEA Augusta S.p.A. under the name of VEGOBOND AX® and which may be described by the following formula:

$$nNa_2O \cdot (1-n)K_2O \cdot Al_2O_3 \cdot (2 - 2.5)SiO_2 \cdot (3.5 - 5.5)\ H_2O.$$

The zeolite may be used both as a builder in a granular compound and as a kind of "powder" to be applied to the entire mixture to be tabletted, both routes normally being used to incorporate the zeolite in the premix.

Suitable zeolites have a mean particle size of less than 10 μm (volume distribution, as measured by the Coulter Counter Method) and contain preferably 18 to 22% by weight and more preferably 20 to 22% by weight of bound water.

The generally known phosphates may of course also be used as builders providing their use should not be avoided on ecological grounds. Among the large number of commercially available phosphates, alkali metal phosphates have the greatest importance in the detergent industry, pentasodium triphosphate and pentapotassium triphosphate (sodium and potassium tripolyphosphate) being particularly preferred.

"Alkali metal phosphates" is the collective term for the alkali metal (more particularly sodium and potassium) salts of the various phosphoric acids, including metaphosphoric acids $(HPO_3)_n$ and orthophosphoric acid (H_3PO_4) and representatives of higher molecular weight. The phosphates combine several advantages: they act as alkalinity sources, prevent lime deposits on machine parts and lime incrustations in fabrics and, in addition, contribute towards the cleaning effect.

Sodium dihydrogen phosphate (NaH_2PO_4) exists as the dihydrate (density 1.91 gcm^{-3}, melting point 60°) and as the monohydrate (density 2.04 gcm^{-3}). Both salts are white readily water-soluble powders which, on heating, lose the water of crystallization and, at 200°C, are converted into the weakly acidic diphosphate (disodium hydrogen diphosphate, $Na_2H_2P_2O_7$) and, at higher temperatures, into sodium trimetaphosphate $(Na_3P_3O_9)$ and Maddrell's salt (see below). NaH_2PO_4 shows an acidic reaction. It is formed by adjusting phosphoric acid with sodium hydroxide to a pH value of 4.5 and spraying the resulting "mash". Potassium dihydrogen phosphate (primary or monobasic potassium phosphate, potassium biphosphate, KDP), KH_2PO_4, is a white salt with a density of 2.33 gcm^{-3}, has a melting point of 253° [decomposition with formation of potassium polyphosphate $(KPO_3)_x$] and is readily soluble in water.

Disodium hydrogen phosphate (secondary sodium phosphate), Na_2HPO_4, is a colorless, readily water-soluble crystalline salt. It exists in water-free form and with 2 moles (density 2.066 gcm^{-3}, water loss at 95°), 7 moles (density 1.68 gcm^{-3}, melting point 48° with loss of 5 H_2O) and 12 moles of water (density 1.52 gcm^{-3}, melting point 35° with loss of 5 H_2O), becomes water-free at 100° and, on fairly intensive heating, is converted into the diphosphate $Na_4P_2O_7$. Disodium hydrogen phosphate is prepared by neutralization of phosphoric acid with soda solution using phenolphthalein as indicator. Dipotassium hydrogen phosphate (secondary or dibasic potassium phosphate), K_2HPO_4, is an amorphous white salt which is readily soluble in water.

Trisodium phosphate, tertiary sodium phosphate, Na_3PO_4, consists of colorless crystals which have a density of 1.62 gcm^{-3} and a melting point of 73-76° (decomposition) as the dodecahydrate, a melting point of 100° as the decahydrate (corresponding to 19-20% P_2O_5) and a density of 2.536 gcm^{-3} in water-free form (corresponding to 39-40% P_2O_5). Trisodium phosphate is readily soluble in water through an alkaline reaction and is prepared by concentrating a solution of exactly 1 mole of disodium phosphate and 1 mole of NaOH by evaporation. Tripotassium phosphate (tertiary or tribasic potassium phosphate), K_3PO_4, is a white deliquescent granular powder with a density of 2.56 gcm^{-3}, has a melting of 1340° and is readily soluble in water through an alkaline reaction. It is formed, for example, when Thomas slag is heated with coal and potassium sulfate. Despite their higher price, the more readily soluble and therefore highly effective potassium phosphates are often preferred to corresponding sodium compounds in the detergent industry.

Tetrasodium diphosphate (sodium pyrophosphate), $Na_4P_2O_7$, exists in water-free form (density 2.534 gcm^{-3}, melting point 988°, a figure of 880° has also been mentioned) and as the decahydrate (density 1.815 - 1.836 gcm^{-3}, melting point 94° with loss of water). Both substances are

colorless crystals which dissolve in water through an alkaline reaction. $Na_4P_2O_7$ is formed when disodium phosphate is heated to >200° or by reacting phosphoric acid with soda in a stoichiometric ratio and spray-drying the solution. The decahydrate complexes heavy metal salts and hardness salts and, hence, reduces the hardness of water. Potassium diphosphate (potassium pyrophosphate), $K_4P_2O_7$, exists in the form of the trihydrate and is a colorless hygroscopic powder with a density of 2.33 gcm^{-3} which is soluble in water, the pH value of a 1% solution at 25° being 10.4.

Relatively high molecular weight sodium and potassium phosphates are formed by condensation of NaH_2PO_4 or KH_2PO_4. They may be divided into cyclic types, namely the sodium and potassium metaphosphates, and chain types, the sodium and potassium polyphosphates. The chain types in particular are known by various different names: fused or calcined phosphates, Graham's salt, Kurrol's salt and Maddrell's salt. All higher sodium and potassium phosphates are known collectively as condensed phosphates.

The industrially important pentasodium triphosphate, $Na_5P_3O_{10}$ (sodium tripolyphosphate), is a non-hygroscopic white water-soluble salt which crystallizes without water or with 6 H_2O and which has the general formula $NaO\text{-}[P(O)(ONa)\text{-}O]_n\text{-}Na$ where n = 3. Around 17 g of the salt free from water of crystallization dissolve in 100 g of water at room temperature, around 20 g at 60° and around 32 g at 100°. After heating of the solution for 2 hours to 100°, around 8% orthophosphate and 15% diphosphate are formed by hydrolysis. In the preparation of pentasodium triphosphate, phosphoric acid is reacted with soda solution or sodium hydroxide in a stoichiometric ratio and the solution is spray-dried. Similarly to Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves many insoluble metal compounds (including lime soaps, etc.). Pentapotassium triphosphate, $K_5P_3O_{10}$ (potassium tripolyphosphate), is marketed for

example in the form of a 50% by weight solution (> 23% P_2O_5, 25% K_2O). The potassium polyphosphates are widely used in the detergent industry. Sodium potassium tripolyphosphates, which may also be used in accordance with the invention, also exist. They are formed for example when sodium trimetaphosphate is hydrolyzed with KOH:

$$(NaPO_3)_3 + 2\ KOH \rightarrow Na_3K_2P_3O_{10} + H_2O$$

According to the invention, they may be used in exactly the same way as sodium tripolyphosphate, potassium tripolyphosphate or mixtures thereof. Mixtures of sodium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of potassium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of sodium tripolyphosphate and potassium tripolyphosphate and sodium potassium tripolyphosphate may also be used in accordance with the invention.

Organic cobuilders suitable for use in the basic tablets according to the invention are, in particular, polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, polyacetals, dextrins, other organic cobuilders (see below) and phosphonates. These classes of substances are described in the following.

Useful organic builders are, for example, the polycarboxylic acids usable, for example, in the form of their sodium salts, polycarboxylic acids in this context being understood to be carboxylic acids which bear more than one acid function. Examples of such carboxylic acids are citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), providing their use is not ecologically unsafe, and mixtures thereof. Preferred salts are the salts of the polycarboxylic acids, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

The acids per se may also be used. Besides their builder effect, the acids also typically have the property of an acidifying component and, hence, also serve to establish a relatively low and mild pH value in detergents. Citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and mixtures thereof are particularly mentioned in this regard.

Other suitable builders are polymeric polycarboxylates such as, for example, the alkali metal salts of polyacrylic or polymethacrylic acid, for example those with a relative molecular weight of 500 to 70,000 g/mole.

The molecular weights mentioned in this specification for polymeric polycarboxylates are weight-average molecular weights M_w of the particular acid form which, basically, were determined by gel permeation chromatography (GPC) using a UV detector. The measurement was carried out against an external polyacrylic acid standard which provides realistic molecular weight values by virtue of its structural similarity to the polymers investigated. These values differ distinctly from the molecular weights measured against polystyrene sulfonic acids as standard. The molecular weights measured against polystyrene sulfonic acids are generally higher than the molecular weights mentioned in this specification.

Particularly suitable polymers are polyacrylates which preferably have a molecular weight of 2,000 to 20,000 g/mole. By virtue of their superior solubility, preferred representatives of this group are the short-chain polyacrylates which have molecular weights of 2,000 to 10,000 g/mole and, more particularly, 3,000 to 5,000 g/mole.

Also suitable are copolymeric polycarboxylates, particularly those of acrylic acid with methacrylic acid and those of acrylic acid or methacrylic acid with maleic acid. Acrylic acid/maleic acid copolymers containing 50 to 90% by weight of acrylic acid and 50 to 10% by weight of maleic acid have proved to be particularly suitable. Their relative molecular weights, based on the free acids, are generally in the range from 2,000 to 70,000 g/mole, preferably in the range from 20,000 to 50,000 g/mole and more preferably

in the range from 30,000 to 40,000 g/mole.

The (co)polymeric polycarboxylates may be used either in powder form or in the form of an aqueous solution. The content of (co)polymeric polycarboxylates in the detergent is preferably from 0.5 to 20% by weight and more preferably from 3 to 10% by weight.

In order to improve solubility in water, the polymers may also contain allyl sulfonic acids, such as allyloxybenzene sulfonic acid and methallyl sulfonic acid, as monomer.

Other particularly preferred polymers are biodegradable polymers of more than two different monomer units, for example those which contain salts of acrylic acid and maleic acid and vinyl alcohol or vinyl alcohol derivatives as monomers or those which contain salts of acrylic acid and 2-alkylallyl sulfonic acid and sugar derivatives as monomers.

Other preferred copolymers are those which are described in German patent applications **DE-A-43 03 320** and **DE-A-44 17 734** and which preferably contain acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers.

Other preferred builders are polymeric aminodicarboxylic acids, salts or precursors thereof. Particular preference is attributed to polyaspartic acids or salts and derivatives thereof which, according to German patent application **DE-A-195 40 086**, are also said to have a bleach-stabilizing effect in addition to their co-builder properties.

Other suitable builders are polyacetals which may be obtained by reaction of dialdehydes with polyol carboxylic acids containing 5 to 7 carbon atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes, such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids, such as gluconic acid and/or glucoheptonic acid.

Other suitable organic builders are dextrins, for example oligomers or polymers of carbohydrates which may be obtained by partial hydrolysis

of starches. The hydrolysis may be carried out by standard methods, for example acid- or enzyme-catalyzed methods. The end products are preferably hydrolysis products with average molecular weights of 400 to 500,000 g/mole. A polysaccharide with a dextrose equivalent (DE) of 0.5 to 40 and, more particularly, 2 to 30 is preferred, the DE being an accepted measure of the reducing effect of a polysaccharide by comparison with dextrose which has a DE of 100. Both maltodextrins with a DE of 3 to 20 and dry glucose sirups with a DE of 20 to 37 and also so-called yellow dextrins and white dextrins with relatively high molecular weights of 2,000 to 30,000 g/mole may be used.

The oxidized derivatives of such dextrins are their reaction products with oxidizing agents which are capable of oxidizing at least one alcohol function of the saccharide ring to the carboxylic acid function. Dextrins thus oxidized and processes for their production are known, for example, from European patent applications **EP-A-0 232 202, EP-A-0 427 349, EP-A-0 472 042** and **EP-A-0 542 496** and from International patent applications **WO 92/18542, WO 93/08251, WO 93/16110, WO 94/28030, WO 95/07303, WO 95/12619** and **WO 95/20608**. An oxidized oligosaccharide corresponding to German patent application **DE-A-196 00 018** is also suitable. A product oxidized at C_6 of the saccharide ring can be particularly advantageous.

Other suitable co-builders are oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate. Ethylenediamine-N,N'-disuccinate (EDDS) is preferably used in the form of its sodium or magnesium salts. Glycerol disuccinates and glycerol trisuccinates are also preferred in this connection. The quantities used in zeolite-containing and/or silicate-containing formulations are from 3 to 15% by weight.

Other useful organic co-builders are, for example, acetylated hydroxycarboxylic acids and salts thereof which may optionally be present in lactone form and which contain at least 4 carbon atoms, at least one

hydroxy group and at most two acid groups. Co-builders such as these are described, for example, in International patent application **WO 95/20029**.

Another class of substances with co-builder properties are the phosphonates, more particularly hydroxyalkane and aminoalkane phosphonates. Among the hydroxyalkane phosphonates, 1-hydroxyethane-1,1-diphosphonate (HEDP) is particularly important as a co-builder. It is preferably used in the form of the sodium salt, the disodium salt showing a neutral reaction and the tetrasodium salt an alkaline reaction (pH 9). Preferred aminoalkane phosphonates are ethylenediamine tetramethylene phosphonate (EDTMP), diethylenetriamine pentamethylenephosphonate (DTPMP) and higher homologs thereof. They are preferably used in the form of the neutrally reacting sodium salts, for example as the hexasodium salt of EDTMP or as the hepta- and octasodium salts of DTPMP. Of the phosphonates, HEDP is preferably used as a builder. In addition, the aminoalkane phosphonates have a pronounced heavy metal binding capacity. Accordingly, it can be of advantage, particularly where the detergents also contain bleach, to use aminoalkane phosphonates, more particularly DTPMP, or mixtures of the phosphonates mentioned.

In addition, any compounds capable of forming complexes with alkaline earth metal ions may be used as co-builders.

The quantity of builder used is normally between 10 and 70% by weight, preferably between 15 and 60% by weight and more preferably between 20 and 50% by weight. The quantity of builder used is again dependent upon the particular application envisaged, so that bleach tablets can contain larger quantities of builders (for example between 20 and 70% by weight, preferably between 25 and 65% by weight and more preferably between 30 and 55% by weight) than, for example, laundry detergent tablets (normally 10 to 50% by weight, preferably 12.5 to 45% by weight and more preferably 17.5 to 37.5% by weight).

Preferred basic tablets additionally contain one or more

surfactant(s). Anionic, nonionic, cationic and/or amphoteric surfactants or mixtures thereof may be used in the basic tablets according to the invention. Mixtures of anionic and nonionic surfactants are preferred from the performance point of view. The total surfactant content of the tablets is between 5 and 60% by weight, based on tablet weight, surfactant contents above 15% by weight being preferred.

The anionic surfactants used are, for example, those of the sulfonate and sulfate type. Preferred surfactants of the sulfonate type are C_{9-13} alkyl benzenesulfonates, olefin sulfonates, i.e. mixtures of alkene and hydroxy-alkane sulfonates, and the disulfonates obtained, for example, from C_{12-18} monoolefins with an internal or terminal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Other suitable surfactants of the sulfonate type are the alkane sulfonates obtained from C_{12-18} alkanes, for example by sulfochlorination or sulfoxidation and subsequent hydrolysis or neutralization. The esters of α-sulfofatty acids (ester sulfonates), for example the α-sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow acids, are also suitable.

Other suitable anionic surfactants are sulfonated fatty acid glycerol esters, i.e. the monoesters, diesters and triesters and mixtures thereof which are obtained where production is carried out by esterification of a monoglycerol with 1 to 3 moles of fatty acid or in the transesterification of triglycerides with 0.3 to 2 moles of glycerol. Preferred sulfonated fatty acid glycerol esters are the sulfonation products of saturated C_{6-22} fatty acids, for example caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid.

Preferred alk(en)yl sulfates are the alkali metal salts and, in particular, the sodium salts of the sulfuric acid semiesters of C_{12-18} fatty alcohols, for example coconut alcohol, tallow alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or C_{10-20} oxoalcohols and the corresponding semiesters

of secondary alcohols with the same chain length. Other preferred alk(en)yl sulfates are those with the chain length mentioned which contain a synthetic, linear alkyl chain based on a petrochemical and which are similar in their degradation behavior to the corresponding compounds based on oleochemical raw materials. C_{12-16} alkyl sulfates and C_{12-15} alkyl sulfates and also C_{14-15} alkyl sulfates are particularly preferred from the washing performance point of view. Other suitable anionic surfactants are 2,3-alkyl sulfates which may be produced, for example, in accordance with **US 3,234,258** or **US 5,075,041** and which are commercially obtainable as products of the Shell Oil Company under the name of DAN®.

The sulfuric acid monoesters of linear or branched C_{7-21} alcohols ethoxylated with 1 to 6 moles of ethylene oxide, such as 2-methyl-branched C_{9-11} alcohols containing on average 3.5 moles of ethylene oxide (EO) or C_{12-18} fatty alcohols containing 1 to 4 EO, are also suitable. In view of their high foaming capacity, they are normally used in only relatively small quantities, for example in quantities of 1 to 5% by weight, in dishwashing detergents.

Other suitable anionic surfactants are the salts of alkyl sulfosuccinic acid which are also known as sulfosuccinates or as sulfosuccinic acid esters and which represent monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and, more particularly, ethoxylated fatty alcohols. Preferred sulfosuccinates contain C_{8-18} fatty alcohol molecules or mixtures thereof. Particularly preferred sulfosuccinates contain a fatty alcohol molecule derived from ethoxylated fatty alcohols which, considered in isolation, represent nonionic surfactants (for a description, see below). Of these sulfosuccinates, those of which the fatty alcohol molecules are derived from narrow-range ethoxylated fatty alcohols are particularly preferred. Alk(en)yl succinic acid preferably containing 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof may also be used.

Other suitable anionic surfactants are, in particular, soaps. Suitable soaps are, in particular, saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and soap mixtures derived in particular from natural fatty acids, for example coconut, palm kernel or tallow acids.

The anionic surfactants, including the soaps, may be present in the form of their sodium, potassium or ammonium salts and as soluble salts of organic bases, such as mono-, di- or triethanolamine. The anionic surfactants are preferably present in the form of their sodium or potassium salts and, more preferably, in the form of their sodium salts.

Preferred nonionic surfactants are alkoxylated, advantageously ethoxylated, more especially primary alcohols preferably containing 8 to 18 carbon atoms and, on average, 1 to 12 moles of ethylene oxide (EO) per mole of alcohol, in which the alcohol group may be linear or, preferably, methyl-branched in the 2-position or may contain linear and methyl-branched groups in the form of the mixtures typically present in oxoalcohol groups. However, alcohol ethoxylates containing linear groups of alcohols of native origin with 12 to 18 carbon atoms, for example coconut, palm, tallow or oleyl alcohol, and on average 2 to 8 EO per mole of alcohol are particularly preferred. Preferred ethoxylated alcohols include, for example, C_{12-14} alcohols containing 3 EO or 4 EO, C_{9-11} alcohol containing 7 EO, C_{13-15} alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C_{12-18} alcohols containing 3 EO, 5 EO or 7 EO and mixtures thereof, such as mixtures of C_{12-14} alcohol containing 3 EO and C_{12-18} alcohol containing 5 EO. The degrees of ethoxylation mentioned represent statistical mean values which, for a special product, can be a whole number or a broken number. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants, fatty alcohols containing more than 12 EO may also be used, examples including tallow fatty alcohol containing 14 EO, 25 EO, 30 EO or 40 EO.

Suitable other nonionic surfactants are alkyl glycosides with the general formula $RO(G)_x$ where R is a primary, linear or methyl-branched, more particularly 2-methyl-branched, aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms and G stands for a glycose unit containing 5 or 6 carbon atoms, preferably glucose. The degree of oligomerization x, which indicates the distribution of monoglycosides and oligoglycosides, is a number of 1 to 10 and preferably 1.2 to 1.4.

Another class of preferred nonionic surfactants which may be used either as sole nonionic surfactant or in combination with other nonionic surfactants are alkoxylated, preferably ethoxylated or ethoxylated and propoxylated, fatty acid alkyl esters preferably containing 1 to 4 carbon atoms in the alkyl chain, more especially the fatty acid methyl esters which are described, for example, in Japanese patent application **JP 58/217598** or which are preferably produced by the process described in International patent application **WO-A-90/13533**.

Nonionic surfactants of the amine oxide type, for example N-coconutalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and the fatty acid alkanolamide type are also suitable. The quantity in which these nonionic surfactants are used is preferably no more than the quantity in which the ethoxylated fatty alcohols are used and, more preferably, no more than half that quantity.

Other suitable surfactants are polyhydroxyfatty acid amides corresponding to formula (IX):

$$\begin{array}{c} R^1 \\ | \\ R\text{-}CO\text{-}N\text{-}[Z] \end{array} \qquad (IX)$$

in which RCO is an aliphatic acyl group containing 6 to 22 carbon atoms, R^1 is hydrogen, an alkyl or hydroxyalkyl group containing 1 to 4 carbon atoms and [Z] is a linear or branched polyhydroxyalkyl group containing 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxyfatty acid

amides are known substances which may normally be obtained by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of polyhydroxyfatty acid amides also includes compounds corresponding to formula (X):

$$\begin{array}{l} \quad R^1\text{-O-}R^2 \\ \quad \ \ | \\ \text{R-CO-N-[Z]} \end{array} \qquad (X)$$

in which R is a linear or branched alkyl or alkenyl group containing 7 to 12 carbon atoms, R^1 is a linear, branched or cyclic alkyl group or an aryl group containing 2 to 8 carbon atoms and R^2 is a linear, branched or cyclic alkyl group or an aryl group or an oxyalkyl group containing 1 to 8 carbon atoms, C_{1-4} alkyl or phenyl groups being preferred, and [Z] is a linear polyhydroxyalkyl group, of which the alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of that group.

[Z] is preferably obtained by reductive amination of a reduced sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds may then be converted into the required polyhydroxyfatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, for example in accordance with the teaching of International patent application **WO-A-95/07331**.

According to the invention, preferred basic tablets contain anionic and nonionic surfactant(s). Performance-related advantages can arise out of certain quantity ratios in which the individual classes of surfactants are used.

For example, particularly preferred basic tablets are characterized in

that the ratio of anionic surfactant(s) to nonionic surfactant(s) is from 10:1 to 1:10, preferably from 7.5:1 to 1:5 and more preferably from 5:1 to 1:2. Other preferred detergent tablets contain anionic and/or nonionic surfactant(s) and have total surfactant contents above 2.5% by weight, preferably above 5% by weight and more preferably above 10% by weight, based on tablet weight. Other particularly preferred detergent tablets are characterized in that they contain surfactant(s), preferably anionic and/or nonionic surfactant(s), in quantities of 5 to 40% by weight, preferably 7.5 to 35% by weight, more preferably 10 to 30% by weight and most preferably 12.5 to 25% by weight, based on the weight of the tablet.

It can be of advantage from the performance point of view if certain classes of surfactants are missing from certain phases of the basic tablets or from the entire tablet, i.e. from every phase. In another important embodiment of the present invention, therefore, at least one phase of the tablets is free from nonionic surfactants.

Conversely, a positive effect can also be obtained through the presence of certain surfactants in individual phases or in the tablet as a whole, i.e. in every phase. Introducing the alkyl polyglycosides described above has proved to be of particular advantage, so that basic tablets in which at least one phase of the tablet contains alkyl polyglycosides are preferred.

As with the nonionic surfactants, the omission of anionic surfactants from individual phases or from all phases can result in basic tablets which are more suitable for certain applications. Accordingly, detergent tablets where at least one phase of the tablet is free from anionic surfactants are also possible in accordance with the present invention.

In order to facilitate the disintegration of heavily compacted tablets, disintegration aids, so-called tablet disintegrators, may be incorporated in them to shorten their disintegration times. According to **Römpp (9th Edition, Vol. 6, page 4440)** and **Voigt *"Lehrbuch der pharmazeutischen***

***Technologie*" (6th Edition, 1987, pag s 182-184)**, tablet disintegrators or disintegration accelerators are auxiliaries which promote the rapid disintegration of tablets in water or gastric juices and the release of the pharmaceuticals in an absorbable form.

These substances, which are also known as "disintegrators" by virtue of their effect, are capable of undergoing an increase in volume on contact with water so that, on the one hand, their own volume is increased (swelling) and, on the other hand, a pressure can be generated through the release of gases which causes the tablet to disintegrate into relatively small particles. Well-known disintegrators are, for example, carbonate/citric acid systems, although other organic acids may also be used. Swelling disintegration aids are, for example, synthetic polymers, such as polyvinyl pyrrolidone (PVP), or natural polymers and modified natural substances, such as cellulose and starch and derivatives thereof, alginates or casein derivatives.

Preferred basic tablets contain 0.5 to 10% by weight, preferably 3 to 7% by weight and more preferably 4 to 6% by weight of one or more disintegration aids, based on the weight of the tablet.

According to the invention, preferred disintegrators are cellulose-based disintegrators, so that preferred basic tablets contain a cellulose-based disintegrator in quantities of 0.5 to 10% by weight, preferably 3 to 7% by weight and more preferably 4 to 6% by weight. Pure cellulose has the formal empirical composition $(C_6H_{10}O_5)_n$ and, formally, is a β-1,4-polyacetal of cellobiose which, in turn, is made up of two molecules of glucose. Suitable celluloses consist of ca. 500 to 5000 glucose units and, accordingly, have average molecular weights of 50,000 to 500,000. According to the invention, cellulose derivatives obtainable from cellulose by polymer-analog reactions may also be used as cellulose-based disintegrators. These chemically modified celluloses include, for example, products of esterification or etherification reactions in which hydroxy

hydrogen atoms have been substituted. However, celluloses in which the hydroxy groups have been replaced by functional groups that are not attached by an oxygen atom may also be used as cellulose derivatives. The group of cellulose derivatives includes, for example, alkali metal celluloses, carboxymethyl cellulose (CMC), cellulose esters and ethers and aminocelluloses. The cellulose derivatives mentioned are preferably not used on their own, but rather in the form of a mixture with cellulose as cellulose-based disintegrators. The content of cellulose derivatives in mixtures such as these is preferably below 50% by weight and more preferably below 20% by weight, based on the cellulose-based disintegrator. In one particularly preferred embodiment, pure cellulose free from cellulose derivatives is used as the cellulose-based disintegrator.

The cellulose used as disintegration aid is preferably not used in fine-particle form, but is converted into a coarser form, for example by granulation or compacting, before it is added to and mixed with the premixes to be tabletted. Detergent tablets which contain granular or optionally co-granulated disintegrators are described in German patent applications **DE 197 09 991** (Stefan Herzog) and **DE 197 10 254** (Henkel) and in International patent application **WO 98/40463** (Henkel). Further particulars of the production of granulated, compacted or co-granulated cellulose disintegrators can also be found in these patent applications. The particle sizes of such disintegration aids is mostly above 200 µm, preferably at least 90% by weight of the particles being between 300 and 1600 µm in size and, more particularly, between 400 and 1200 µm in size. According to the invention, the above-described relatively coarse-particle cellulose-based disintegrators described in detail in the cited patent applications are preferably used as disintegration aids and are commercially obtainable, for example under the name of Arbocel® TF-30-HG from Rettenmaier.

Microcrystalline cellulose may be used as another cellulose-based

disintegration aid or as part of such a component. This microcrystalline cellulose is obtained by partial hydrolysis of the celluloses under conditions which only attack and completely dissolve the amorphous regions (ca. 30% of the total cellulose mass) of the celluloses, but leave the crystalline regions (ca. 70%) undamaged. Subsequent de-aggregation of the microfine celluloses formed by hydrolysis provides the microcrystalline celluloses which have primary particle sizes of ca. 5 µm and which can be compacted, for example, to granules with a mean particle size of 200 µm.

According to the invention, preferred detergent tablets aditionally contain a disintegration aid, preferably a cellulose-based disintegration aid, preferably in granular, co-granulated or compacted form, in quantities of 0.5 to 10% by weight, preferably in quantities of 3 to 7% by weight and more preferably in quantities of 4 to 6% by weight, based on tablet weight, preferred disintegration aids having mean particle sizes above 300 µm, preferably above 400 µm and more preferably above 500 µm.

Besides the ingredients mentioned thus far (builder, surfactant and disintegration aid), the detergent tablets according to the invention may contain other typical detergent ingredients from the group of bleaching agents, bleach activators, dyes, perfumes, optical brighteners, enzymes, foam inhibitors, silicone oils, redeposition inhibitors, discoloration inhibitors, dye transfer inhibitors and corrosion inhibitors.

To develop the required bleaching effect, the detergent tablets according to the invention may contain bleaching agents. The usual bleaching agents from the group consisting of sodium perborate monohydrate, sodium perborate tetrahydrate and sodium percarbonate have proved to be particularly useful in this regard.

"Sodium percarbonate" is a non-specific term used for sodium carbonate peroxohydrates which, strictly speaking, are not "percarbonates" (i.e. salts of percarbonic acid), but hydrogen peroxide adducts with sodium carbonate. The commercial material has the mean composition 2 Na_2CO_3 ·

3 H_2O_2 and, accordingly, is not a peroxycarbonate. Sodium percarbonate forms a white water-soluble powder with a density of 2.14 gcm^{-3} which readily decomposes into sodium carbonate and bleaching or oxidizing oxygen.

Sodium carbonate peroxohydrate was obtained for the first time in 1899 by precipitation with ethanol from a solution of sodium carbonate in hydrogen peroxide, but was mistakenly regarded as peroxycarbonate. It was only in 1909 that the compound was recognised as a hydrogen peroxide addition compound. Nevertheless, the historical name "sodium percarbonate" has been adopted in practice.

On an industrial scale, sodium percarbonate is mainly produced by precipitation from aqueous solution (so-called wet process). In this process, aqueous solutions of sodium carbonate and hydrogen peroxide are combined and the sodium percarbonate is precipitated by salting-out agents (mainly sodium chloride), crystallization aids (for example polyphosphates, polyacrylates) and stabilizers (for example Mg^{2+} ions). The precipitated salt which still contains 5 to 12% by weight of mother liquor is then removed by centrifuging and dried at 90°C in fluidized bed dryers. The bulk density of the end product can vary between 800 and 1200 g/l according to the production process. In general, the percarbonate is stabilized by an additional coating. Coating processes and materials are widely described in the patent literature. Basically, any commercially available percarbonate types as marketed, for example, by Solvay Interox, Degussa, Kemira and Akzo may be used in accordance with the present invention.

So far as the bleaching agents used are concerned, the content of these substances in the tablets is determined by the application envisaged for the tablets. Whereas conventional heavy-duty detergents in tablet form contain between 5 and 30% by weight, preferably between 7.5 and 25% by weight and more preferably between 12.5 and 22.5% by weight of

bleaching agent, bleach or bleach booster tablets contain between 15 and 50% by weight, preferably between 22.5 and 45% by weight and more preferably between 30 and 40% by weight.

In addition to the bleaching agents used, the detergent tablets according to the invention may contain bleach activator(s) which represents a preferred embodiment of the present invention. Bleach activators are incorporated in detergents in order to obtain an improved bleaching effect at washing temperatures of 60°C or lower. According to the invention, compounds which form aliphatic peroxocarboxylic acids preferably containing 1 to 10 carbon atoms and more preferably 2 to 4 carbon atoms and/or optionally substituted perbenzoic acid under perhydrolysis conditions may be used as bleach activators. Suitable bleach activators are substances which contain O- and/or N-acyl groups with the number of carbon atoms indicated and/or optionally substituted benzoyl groups. Preferred additional bleach activators are polyacylated alkylenediamines, more especially tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, more particularly 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycol urils, more particularly tetraacetyl glycol uril (TAGU), N-acylimides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl- or isononanoyl-oxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, more especially phthalic anhydride, acylated polyhydric alcohols, more especially triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran.

In addition to or instead of the conventional bleach activators, so-called bleach catalysts may also be incorporated in the tablets. Bleach catalysts are bleach-boosting transition metal salts or transition metal complexes such as, for example, Mn-, Fe-, Co-, Ru- or Mo-salen complexes or carbonyl complexes. Mn-, Fe-, Co-, Ru-, Mo-, Ti-, V- and Cu-complexes with N-containing tripod ligands and Co-, Fe-, Cu- and Ru-ammine complexes may also be used as bleach catalysts.

If the tablets according to the invention contain bleach activators, they contain between 0.5 and 30% by weight, preferably between 1 and 20% by weight and more preferably between 2 and 15% by weight - based on the tablet as a whole - of one or more bleach activators or bleach catalysts. These quantities may vary according to the application envisaged for the tablets. Thus, in typical heavy-duty detergent tablets, bleach activator contents of 0.5 to 10% by weight, preferably 2 to 8% by weight and more preferably 4 to 6% by weight are normal whereas bleach tablets can have much higher contents, for example between 5 and 30% by weight, preferably between 7.5 and 25% by weight and more preferably between 10 and 20% by weight. The expert is not restricted in his freedom of formulation and is able in this way to produce laundry detergent tablets, dishwasher tablets or bleach tablets with a stronger or weaker bleaching effect by varying the contents of bleach activator and bleaching agent.

A particularly preferred bleach activator is N,N,N',N'-tetraacetyl ethylenediamine which is widely used in laundry/dishwasher detergents. Accordingly, preferred detergent tablets are characterized in that they contain tetraacetyl ethylenediamine in the quantities mentioned above as bleach activator.

Besides the ingredients mentioned (bleaching agent, bleach activator, builder, surfactant and disintegration aid), the detergent tablets according to the invention may contain other ingredients typical of detergents from the group of dyes, perfumes, optical brighteners, enzymes foam inhibitors, silicone oils, redeposition inhibitors, discoloration inhibitors, dye transfer inhibitors and corrosion inhibitors.

In order to improve their aesthetic impression, the detergents according to the invention may be colored with suitable dyes. Preferred dyes, which are not difficult for the expert to choose, have high stability in storage, are not affected by the other ingredients of the detergents or by light and do not have any pronounced substantivity for textile fibers so as

not to color them.

Any dyes which can be destroyed by oxidation in the washing process and mixtures thereof with suitable blue dyes, so-called blueing agents, are preferably used in the detergent tablets according to the invention. It has proved to be of advantage to use dyes which are soluble in water or - at room temperature - in liquid organic substances. Suitable dyes are, for example, anionic dyes, for example anionic nitroso dyes. One possible dye is, for example, naphthol green (Color Index (CI) Part 1: Acid Green 1; Part 2: 10020), which is commercially available for example as Basacid® Grün 970 from BASF, Ludwigshafen, and mixtures thereof with suitable blue dyes. Other suitable dyes are Pigmosol® Blau 6900 (CI 74160), Pigmosol® Grün 8730 (CI 74260), Basonyl® Rot 545 FL (CI 45170), Sandolan® Rhodamin EB 400 (CI 45100), Basacid® Gelb 094 (CI 47005), Sicovit® Patentblau 85 E 131 (CI 42051), Acid Blue 183 (CAS 12217-22-0, CI Acid Blue 183), Pigment Blue 15 (CI 74160), Supranol® Blau GLW (CAS 12219-32-8, CI Acid Blue 221)), Nylosan® Gelb N-7GL SGR (CAS 61814-57-1, CI Acid Yellow 218) and/or Sandolan® Blau (CI Acid Blue 182, CAS 12219-26-0).

In selecting the dye, it is important to ensure that the dye does not have an excessive affinity for the textile surfaces and, in particular, for synthetic fibers. Another factor to be taken into account in the selection of suitable dyes is that dyes differ in their stability to oxidation. Generally speaking, water-insoluble dyes are more stable to oxidation than water-soluble dyes. The concentration of the dye in the detergents varies according to its solubility and hence its sensitivity to oxidation. In the case of readily water-soluble dyes, for example the above-mentioned Basacid® Grün and Sandolan® Blau, dye concentrations in the range from a few 10^{-2} to 10^{-3} % by weight are typically selected. By contrast, in the case of the pigment dyes which are particularly preferred for their brilliance, but which are less readily soluble in water, for example the above-mentioned

Pigmosol® dyes, suitable concentrations of the dye in detergents are typically of the order of a few 10^{-3} to 10^{-4} % by weight.

The tablets may contain derivatives of diaminostilbenedisulfonic acid or alkali metal salts thereof as optical brighteners. Suitable optical brighteners are, for example, salts of 4,4'-bis-(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)-stilbene-2,2'-disulfonic acid or compounds of similar composition which contain a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. Brighteners of the substituted diphenyl styryl type, for example alkali metal salts of 4,4'-bis-(2-sulfostyryl)-diphenyl, 4,4'-bis-(4-chloro-3-sulfostyryl)-diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)-diphenyl, may also be present. Mixtures of the brighteners mentioned above may also be used. The optical brighteners are used in the detergent tablets according to the invention in concentrations of 0.01 to 1% by weight, preferably 0.05 to 0.5% by weight and more preferably 0.1 to 0.25% by weight, based on the tablet as a whole.

Perfumes are added to the detergent tablets according to the invention to improve the aesthetic impression created by the products and to provide the consumer not only with the required washing performance but also with a visually and sensorially "typical and unmistakable" product. Suitable perfume oils or perfumes include individual perfume compounds, for example synthetic products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Perfume compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl cyclohexyl acetate, linalyl acetate, dimethyl benzyl carbinyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, ethyl methyl phenyl glycinate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen

aldehyde, hydroxycitronellal, lilial and bourgeonal; the ketones include, for example, the ionones, α-isomethyl ionone and methyl cedryl ketone; the alcohols include anethol, citronellol, eugenol, geraniol, linalool, phenyl ethyl alcohol and terpineol and the hydrocarbons include, above all, the terpenes, such as limonene and pinene. However, mixtures of various perfumes which together produce an attractive perfume note are preferably used. Perfume oils such as these may also contain natural perfume mixtures obtainable from vegetable sources, for example pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. Also suitable are clary oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil and labdanum oil and orange blossom oil, neroli oil, orange peel oil and sandalwood oil.

The detergent tablets according to the invention normally contain up to 2% by weight of perfumes, based on the formulation as a whole. The perfumes may be directly incorporated in the detergents according to the invention, although it can also be of advantage to apply the perfumes to supports which strengthen the adherence of the perfume to the washing and which provide the textiles with a long-lasting fragrance through a slower release of the perfume. Suitable support materials are, for example, cyclodextrins, the cyclodextrin/perfume complexes optionally being coated with other auxiliaries.

Suitable enzymes are, in particular, those from the classes of hydrolases, such as proteases, esterases, lipases or lipolytic enzymes, amylases, cellulases or other glycosyl hydrolases and mixtures thereof. All these hydrolases contribute to the removal of stains, such as protein-containing, fat-containing or starch-containing stains, and discoloration in the washing process. Cellulases and other glycosyl hydrolases can contribute towards color retention and towards increasing fabric softness by removing pilling and microfibrils. Oxidoreductases may also be used for bleaching and for inhibiting dye transfer. Enzymes obtained from bacterial

strains or fungi, such as Bacillus subtilis, Bacillus licheniformis, Streptomyces griseus, Coprinus cinereus and Humicola insolens and from genetically modified variants are particularly suitable. Proteases of the subtilisin type are preferably used, proteases obtained from Bacillus lentus being particularly preferred. Of particular interest in this regard are enzyme mixtures, for example of protease and amylase or protease and lipase or lipolytic enzymes or protease and cellulase or of cellulase and lipase or lipolytic enzymes or of protease, amylase and lipase or lipolytic enzymes or protease, lipase or lipolytic enzymes and cellulase, but especially protease- and/or lipase-containing mixtures or mixtures with lipolytic enzymes. Examples of such lipolytic enzymes are the known cutinases. Peroxidases or oxidases have also been successfully used in some cases. Suitable amylases include in particular α-amylases, isoamylases, pullanases and pectinases. Preferred cellulases are cellobiohydrolases, endoglucanases and β-glucosidases, which are also known as cellobiases, and mixtures thereof. Since the various cellulase types differ in their CMCase and avicelase activities, the desired activities can be established by mixing the cellulases in the appropriate ratios.

The enzymes may be adsorbed to supports and/or encapsulated in membrane materials to protect them against premature decomposition. The percentage content of the enzymes, enzyme mixtures or enzyme granules may be, for example, from about 0.1 to 5% by weight and is preferably from 0.5 to about 4.5% by weight.

In addition, the detergent tablets according to the invention may also contain components with a positive effect on the removability of oil and fats from textiles by washing (so-called soil repellents). This effect becomes particularly clear when a textile which has already been repeatedly washed with a detergent according to the invention containing this oil- and fat-dissolving component is soiled. Preferred oil- and fat-dissolving components include, for example, nonionic cellulose ethers, such as methyl

cellulose and methyl hydroxypropyl cellulose containing 15 to 30% by weight of methoxyl groups and 1 to 15% by weight of hydroxypropoxyl groups, based on the nonionic cellulose ether, and the polymers of phthalic acid and/or terephthalic acid known from the prior art or derivatives thereof, more particularly polymers of ethylene terephthalates and/or polyethylene glycol terephthalates or anionically and/or nonionically modified derivatives thereof. Of these, the sulfonated derivatives of phthalic acid and terephthalic acid polymers are particularly preferred.

The tablets according to the invention are produced in two steps. In the first step, detergent tablets are produced in known manner by tabletting particulate detergent compositions and, in the second step, are provided with the coating.

Accordingly, the present invention relates to a process for the production of coated detergent tablets by tabletting a particulate detergent composition in known manner and then dipping the resulting tablets in or spraying them with a melt, solution or dispersion of one or more polymers from the group of

a) water-soluble nonionic polymers from the group of

a1) polyvinyl pyrrolidones,

a2) vinyl pyrrolidone/vinyl ester copolymers,

a3) cellulose ethers

b) water-soluble amphoteric polymers from the group of

b1) alkyl acrylamide/acrylic acid copolymers,

b2) alkyl acrylamide/methacrylic acid copolymers,

b3) alkyl acrylamide/methyl methacrylic acid copolymers,

b4) alkyl acrylamide/acrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b5) alkyl acrylamide/methacrylic acid/alkylaminoalkyl (meth)acrylic acid

copolymers,

b6) alkyl acrylamide/methyl methacrylic acid/alkylaminoalkyl (meth)-acrylic acid copolymers,

b7) alkyl acrylamide/alkyl methacrylate/alkylaminoethyl methacrylate/alkyl methacrylate copolymers,

b8) copolymers of

b8i) unsaturated carboxylic acids,

b8ii) cationically derivatized unsaturated carboxylic acids,

b8iii) optionally other ionic or nonionic monomers,

c) water-soluble zwitterionic polymers from the group of

c1) acrylamidoalkyl trialkylammonium chloride/acrylic acid copolymers and alkali metal and ammonium salts thereof,

c2) acrylamidoalkyl trialkylammonium chloride/methacrylic acid copolymers and alkali metal and ammonium salts thereof,

c3) methacroyl ethyl betaine/methacrylate copolymers,

d) water-soluble anionic polymers from the group of

d1) vinyl acetate/crotonic acid copolymers,

d2) vinyl pyrrolidone/vinyl acrylate copolymers,

d3) acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,

d4) graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or polyalkylene glycols,

d5) grafted and crosslinked copolymers from the copolymerization of

d5i) at least one monomer of the nonionic type,

d5ii) at least one monomer of the ionic type,

d5iii) polyethylene glycol and

d5iv) a crosslinking agent,

d6) copolymers obtained by copolymerization of at least one monomer of each of the following three groups:

d6i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,

d6ii) unsaturated carboxylic acids,

d6iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group d6ii) with saturated or unsaturated, linear or branched C_{8-18} alcohols,

d7) terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl ester,

d8) tetrapolymers and pentapolymers of

d8i) crotonic acid or allyloxyacetic acid,

d8ii) vinyl acetate or vinyl propionate,

d8iii) branched allyl or methallyl esters,

d8iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters,

d9) crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinyl benzene, vinyl methyl ether, acrylamide and water-soluble salts thereof,

d10) terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic monocarboxylic acid branched in the α-position,

e) water-soluble cationic polymers from the group of

e1) quaternized cellulose derivatives,

e2) polysiloxanes containing quaternary groups,

e3) cationic guar derivatives,

e4) polymeric dimethyl diallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid,

e5) copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate,

e6) vinyl pyrrolidone/methoimidazolinium chloride copolymers,

e7) quaternized polyvinyl alcohol,

e8) polymers known by the INCI names of polyquaternium 2, polyquaternium 17, polyquaternium 18 and polyquaternium 27.

Analogously to the foregoing observations on the detergent tablets according to the invention, the polymers mentioned are also preferred for the process according to the invention, so that reference may be made to the foregoing observations.

The two key process steps are described in the following.

The tablets to be subsequently coated in accordance with the invention according to the invention are produced by first dry-mixing the ingredients - which may be completely or partly pregranulated - and then shaping/forming, morre particularly tabletting, the resulting mixture using conventional processes. To produce the tablets according to the invention, the premix is compacted between two punches in a die to form a solid compactate. This process, which is referred to in short hereinafter as tabletting, comprises four phases, namely metering, compacting (elastic deformation), plastic deformation and ejection.

The premix is first introduced into the die, the filling level and hence the weight and shape of the tablet formed being determined by the position of the lower punch and the shape of the die. Uniform dosing, even at high tablet throughputs, is preferably achieved by volumetric dosing of the premix. As the tabletting process continues, the top punch comes into contact with the premix and continues descending towards the bottom punch. During this compaction phase, the particles of the premix are pressed closer together, the void volume in the filling between the punches continuously diminishing. The plastic deformation phase in which the particles coalesce and form the tablet begins from a certain position of the

top punch (and hence from a certain pressure on the premix). Depending on the physical properties of the premix, its constituent particles are also partly crushed, the premix sintering at even higher pressures. As the tabletting rate increases, i.e. at high throughputs, the elastic deformation phase becomes increasingly shorter so that the tablets formed can have more or less large voids. In the final step of the tabletting process, the tablet is forced from the die by the bottom punch and carried away by following conveyors. At this stage, only the weight of the tablet is definitively established because the tablets can still change shape and size as a result of physical processes (re-elongation, crystallographic effects, cooling, etc.).

The tabletting process is carried out in commercially available tablet presses which, in principle, may be equipped with single or double punches. In the latter case, not only is the top punch used to build up pressure, the bottom punch also moves towards the top punch during the tabletting process while the top punch presses downwards. For small production volumes, it is preferred to use eccentric tablet presses in which the punch(es) is/are fixed to an eccentric disc which, in turn, is mounted on a shaft rotating at a certain speed. The movement of these punches is comparable with the operation of a conventional four-stroke engine. Tabletting can be carried out with a top punch and a bottom punch, although several punches can also be fixed to a single eccentric disc, in which case the number of die bores is correspondingly increased. The throughputs of eccentric presses vary according to type from a few hundred to at most 3,000 tablets per hour.

For larger throughputs, rotary tablet presses are generally used. In rotary tablet presses, a relatively large number of dies is arranged in a circle on a so-called die table. The number of dies varies – according to model – between 6 and 55, although even larger dies are commercially available. Top and bottom punches are associated with each die on the

die table, the tabletting pressures again being actively built up not only by the top punch or bottom punch, but also by both punches. The die table and the punches move about a common vertical axis, the punches being brought into the filling, compaction, plastic deformation and ejection positions by means of curved guide rails. At those places where the punches have to be raised or lowered to a particularly significant extent (filling, compaction, ejection), these curved guide rails are supported by additional push-down members, pull-down rails and ejection paths. The die is filled from a rigidly arranged feed unit, the so-called filling shoe, which is connected to a storage container for the premix. The pressure applied to the premix can be individually adjusted through the tools for the top and bottom punches, pressure being built up by the rolling of the punch shank heads past adjustable pressure rollers.

To increase throughput, rotary presses can also be equipped with two filling shoes so that only half a circle has to be negotiated to produce a tablet. To produce two-layer or multiple-layer tablets, several filling shoes are arranged one behind the other without the lightly compacted first layer being ejected before further filling. Given suitable process control, shell and bull's-eye tablets – which have a structure resembling an onion skin – can also be produced in this way. In the case of bull's-eye tablets, the upper surface of the core or rather the core layers is not covered and thus remains visible. Rotary tablet presses can also be equipped with single or multiple punches so that, for example, an outer circle with 50 bores and an inner circle with 35 bores can be simultaneously used for tabletting. Modern rotary tablet presses have throughputs of more than one million tablets per hour.

Where rotary presses are used for tabletting, it has proved to be of advantage to carry out the tabletting process with minimal variations in the weight of the tablets. Variations in tablet hardness can also be reduced in this way. Minimal variations in weight can be achieved as follows:

- using plastic inserts with minimal thickness tolerances
- low rotor speed
- large filling shoe
- adapting the rotational speed of the filling shoe blade to the rotor speed
- filling shoe with constant powder height
- decoupling the filling shoe from the powder supply

Any of the nonstick coatings known in the art may be used to reduce caking on the punch. Plastic coatings, plastic inserts or plastic punches are particularly advantageous. Rotating punches have also proved to be of advantage; if possible, the upper and lower punches should be designed for rotation. If rotating punches are used, there will generally be no need for a plastic insert. In that case, the surfaces of the punch should be electropolished.

It has also been found that long tabletting times are advantageous. These can be achieved by using pressure rails, several pressure rollers or low rotor speeds. Since variations in tablet hardness are caused by variations in the pressures applied, systems which limit the tabletting pressure should be used. Elastic punches, pneumatic compensators or spring elements in the force path may be used. The pressure roller can also be spring-mounted.

Tabletting machines suitable for the purposes of the invention can be obtained, for example, from the following companies: Apparatebau Holzwarth GbR, Asperg; Wilhelm Fette GmbH, Schwarzenbek; Hofer GmbH, Weil; Horn & Noack Pharmatechnik GmbH, Worms; IMA Verpackungssysteme GmbH Viersen; KILIAN, Cologne; KOMAGE, Kell am See, KORSCH Pressen GmbH, Berlin; and Romaco GmbH, Worms. Other suppliers are, for example Dr. Herbert Pete, Vienna (AU); Mapag Maschinenbau AG, Bern (Switzerland); BWI Manesty, Liverpool (GB); I. Holand Ltd., Nottingham (GB); and Courtoy N.V., Halle (BE/LU) and Medicopharm, Kamnik (SI). One example of a particularly suitable

tabletting machine is the model HPF 630 hydraulic double-pressure press manufactured by LAEIS, D. Tabletting tools are obtainable, for example, from Adams Tablettierwerkzeuge Dresden; Wilhelm Fett GmbH, Schwarzenbek; Klaus Hammer, Solingen; Herber & Söhne GmbH, Hamburg; Hofer GmbH, Weil; Horn & Noack, Pharmatechnik GmbH, Worms; Ritter Pharmatechnik GmbH, Hamburg; Romaco GmbH, Worms and Notter Werkzeugbau, Tamm. Other suppliers are, for example, Senss AG, Reinach (CH) and Medicopharm, Kamnik (SI).

The tablets can be made in certain shapes and certain sizes. Suitable shapes are virtually any easy-to-handle shapes, for example slabs, bars, cubes, squares and corresponding shapes with flat sides and, in particular, cylindrical forms of circular or oval cross-section. This last embodiment encompasses shapes from tablets to compact cylinders with a height-to-diameter ratio of more than 1.

The portioned pressings may be formed as separate individual elements which correspond to a predetermined dose of the detergent. However, it is also possible to form pressings which combine several such units in a single pressing, smaller portioned units being easy to break off in particular through the provision of predetermined weak spots. For the use of laundry detergents in machines of the standard European type with horizontally arranged mechanics, it can be of advantage to produce the portioned pressings as cylindrical or square tablets, preferably with a diameter-to-height ratio of about 0.5:2 to 2:0.5. Commercially available hydraulic presses, eccentric presses and rotary presses are particularly suitable for the production of pressings such as these.

The three-dimensional form of another embodiment of the tablets according to the invention is adapted in its dimensions to the dispensing compartment of commercially available domestic washing machines, so that the tablets can be introduced directly, i.e. without a dosing aid, into the dispensing compartment where they dissolve on contact with water.

However, it is of course readily possible - and preferred in accordance with the present invention - to use the detergent tablets in conjunction with a dosing aid.

Another preferred tablet which can be produced has a plate-like or slab-like structure with alternately thick long segments and thin short segments, so that individual segments can be broken off from this "bar" at the predetermined weak spots, which the short thin segments represent, and introduced into the machine. This "bar" principle can also be embodied in other geometric forms, for example vertical triangles which are only joined to one another at one of their longitudinal sides.

In another possible embodiment, however, the various components are not compressed to form a single tablet, instead the tablets obtained comprise several layers, i.e. at least two layers. These various layers may have different dissolving rates. This can provide the tablets with favorable performance properties. If, for example, the tablets contain components which adversely affect one another, one component may be integrated in the more quickly dissolving layer while the other component may be incorporated in a more slowly dissolving layer so that the first component can already have reacted off by the time the second component dissolves. The various layers of the tablets can be arranged in the form of a stack, in which case the inner layer(s) dissolve at the edges of the tablet before the outer layers have completely dissolved. Alternatively, however, the inner layer(s) may also be completely surrounded by the layers lying further to the outside which prevents constituents of the inner layer(s) from dissolving prematurely.

In another preferred embodiment of the invention, a tablet consists of at least three layers, i.e. two outer layers and at least one inner layer, a peroxy bleaching agent being present in at least one of the inner layers whereas, in the case of the stack-like tablet, the two cover layers and, in the case of the envelope-like tablet, the outermost layers are free from

peroxy bleaching agent. In another possible embodiment, peroxy bleaching agent and any bleach activators or bleach catalysts present and/or enzymes may be spatially separated from one another in one and the same tablet. Multilayer tablets such as these have the advantage that they can be used not only via a dispensing compartment or via a dosing unit which is added to the wash liquor, instead it is also possible in cases such as these to introduce the tablet into the machine in direct contact with the fabrics without any danger of spotting by bleaching agent or the like.

Besides the layered structure, multiphase tablets may also be produced in the form of ring/core tablets, core/jacket tablets or so-called bull's-eye tablets. An overview of these various forms of multiphase tablets can be found in **EP 055 100** (Jeyes Group). This document discloses lavatory cleaning blocks comprising a shaped body of a slowly dissolving cleaning composition in which a bleach tablet is embedded. At the same time, it discloses various forms of multiphase tablets from the simple multiphase tablet to complicated multilayer systems with inserts.

After pressing, the detergent tablets have high stability. The fracture resistance of cylindrical tablets can be determined via the diametral fracture stress. This in turn can be determined in accordance with the following equation:

$$\Phi = \frac{2P}{BDt}$$

where Φ represents the diametral fracture stress (DFS) in Pa, P is the force in N which leads to the pressure applied to the tablet that results in fracture thereof, D is the diameter of the tablet in meters and t is its height.

Preferred processes for the production of detergent tablets start out from surfactant-containing granules which are compounded with other ingredients to form a tablettable particulate premix. Analogously to the foregoing observations on preferred ingredients of the detergent tablets

according to the invention, the use of other ingredients may also be applied to their production. In preferred processes, the particulate premix additionally contains surfactant-containing granules and has a bulk density of at least 500 g/l, preferably at least 600 g/l and more preferably at least 700 g/l.

In preferred processes according to the invention, the surfactant-containing granules have particle sizes between 100 and 2000 µm, preferably between 200 and 1800 µm, more preferably between 400 and 1600 µm and most preferably between 600 and 1400 µm.

The other ingredients of the detergent tablets according to the invention may also be introduced into the process according to the invention, for which purpose reference is made to the foregoing observations. Preferred processes are characterized in that the particulate premix additionally contains one or more substances from the group of bleaching agents, bleach activators, disintegration aids, enzymes, pH regulators, perfumes, perfume carriers, fluorescers, dyes, foam inhibitors, silicone oils, redeposition inhibitors, optical brighteners, discoloration inhibitors, dye transfer inhibitors and corrosion inhibitors.

The second step of the process according to the invention comprises applying the coating. This may be done by conventional coating techniques, i.e. in particular dipping the tablet in or spraying the tablet with a melt, solution or dispersion of the polymers mentioned.

Since the dipping of detergent tablets into melts or solutions or dispersions only leads to the thin coatings required with considerable outlay on the necessary equipment, it is preferred in accordance with the present invention to spray polymer solutions or dispersions onto the tablets, the solvent or dispersant evaporating and leaving a coating behind on the tablet. In preferred processes according to the invention, an aqueous solution of one or more polymers from groups a) to e) is sprayed onto the tablets, the aqueous solution containing - based on the solution - 1 to 20%

by weight, preferably 2 to 15% by weight and more preferably 4 to 10% by weight of polymer(s) from groups a) to e), optionally up to 20% by weight, preferably up to 10% by weight and more preferably less than 5% by weight of one or more water-miscible solvents and - for the rest - water.

In order to shorten the drying time, other water-miscible readily volatile solvents may be added to and mixed with the aqueous solution. These solvents belong in particular to the group of alcohols, ethanol, n-propanol and isopropanol being preferred. For reasons of cost, ethanol and isopropanol are particularly appropriate.

The polymers from groups a) to e) make up 50 to 100% by weight of the coating of the tablets according to the invention. Accordingly, the solution to be sprayed onto the tablets may contain other ingredients, an addition of polyurethanes - as mentioned above - being preferred. If water-insoluble polyurethanes are added, the liquid to be sprayed on is a dispersion.

Accordingly, another preferred embodiment of the process according to the invention is a variant in which an aqueous dispersion of one or more polyurethanes additionally containing one or more dissolved polymers from groups a) to e) is sprayed onto the tablets, the dispersion containing - based on the dispersion - 1 to 20% by weight, preferably 2 to 15% by weight and more preferably 4 to 10% by weight of polyurethane(s), 1 to 20% by weight, preferably 2 to 15% by weight and more preferably 4 to 10% by weight of polymer(s) from groups a) to e), optionally up to 20% by weight, preferably up to 10% by weight and more preferably below 5% by weight of one or more water-miscible solvents and - for the rest - water.

Aqueous dispersions in the context of the present invention are dispersions of which the outer phase consists predominantly of water. The outer phase may additionally contain other water-miscible solvents such as, for example, ethanol and isopropanol. These other solvents are present in quantities of at most up to 20% by weight, based on the dispersion as a

whole. The outer phase preferably contains water as sole solvent. Another preferred embodiment contains no more than 5%, based on the dispersion as a whole, of other solvents in the outer phase.

The spraying of aqueous solutions or dispersions of the type in question can be carried out in various ways familiar to the expert. For example, the solution or dispersion may be delivered by means of a pump system to a nozzle where the solution or dispersion is finely atomized under the effect of the powerful shear forces. The spray mist formed can then be directed onto the tablets to be coated which are then optionally dried by suitable measures (for example by blowing heated air onto them). However, it is also possible to use a multicomponent nozzle and to spray the aqueous solutions or dispersions by means of a gas stream through the nozzle. In the most simple case, a two-component nozzle is used with compressed air as the carrier gas. In order to protect the dispersion against oxidation or other interactions with the carrier gas, other carrier gases, for example nitrogen noble gases, lower alkanes or ethers, may also be used.

The water content of the dispersion or solution may also be reduced which shortens the drying times, minimizes interactions with moisture-sensitive ingredients on the tablet surface and reduces production costs. Here, too, the lower alcohols mentioned above represent suitable solvents, solvent mixtures completely free from water being less preferred because certain quantities of water promote the formation of a uniform coating. In preferred processes according to the invention, a solution or dispersion of one or more polymers from groups a) to e) in a solvent or solvent mixture from the group consisting of water, ethanol, propanol, isopropanol, n-heptane and mixtures thereof is sprayed onto the tablets using inert propellents from the group consisting of nitrogen, dinitrogen oxide, propane, butane, dimethyl ether and mixtures thereof.

In preferred process variants such as these, the solutions or

dispersions advantageously have the following composition (the quantities being based on the dispersion to be sprayed on):

i) 30 to 99% by weight, preferably 40 to 90% by weight and more preferably 50 to 85% by weight of ethanol, propanol, isopropanol, n-heptane or mixtures thereof,

ii) 0 to 20% by weight, preferably 1 to 15% by weight and more preferably 2 to 10% by weight of water,

iii) 1 to 50% by weight, preferably 2 to 25% by weight and more preferably 3 to 10% by weight of one or more polymers from groups a) to e).

If polyurethanes or other ingredients are to be part of the coating, they may replace up to 50% by weight, based on the weight mentioned, of the polymers from groups a) to e) in the general formulation mentioned above.

Other ingredients of the dispersions to be sprayed on may be, for example, dyes or perfumes or pigments. Additives such as these improve, for example, the visual or olfactory impression of the tablets coated in accordance with the invention. Dyes and perfumes are described in detail in the foregoing. Suitable pigments are, for example, white pigments, such as titanium dioxide or zinc sulfide, pearlescent pigments or colored pigments. Colored pigments may be divided into inorganic and organic pigments. If they are used, the pigments mentioned are all preferably used in fine-particle form, i.e. with mean particle sizes of 100 µm or far smaller.

In order to obtain a thin, uniform coating, the solution or dispersion of the coating materials is preferably converted into a fine mist before it impinges on the tablets. Preferred processes according to the invention are characterized in that the particular solution and/or dispersion is applied to the tablets through a nozzle, the mean droplet size in the spray mist being less than 100 µm, preferably less than 50 µm and more preferably less than 35 µm. The preferred coating thickness mentioned above can

readily be achieved in this way.

The present invention also relates to the use of polymers or polymer mixtures for coating detergent tablets, the polymer or at least 50% by weight of the polymer mixture being selected from

a) water-soluble nonionic polymers from the group of

a1) polyvinyl pyrrolidones,

a2) vinyl pyrrolidone/vinyl ester copolymers,

a3) cellulose ethers

b) water-soluble amphoteric polymers from the group of

b1) alkyl acrylamide/acrylic acid copolymers,

b2) alkyl acrylamide/methacrylic acid copolymers,

b3) alkyl acrylamide/methyl methacrylic acid copolymers,

b4) alkyl acrylamide/acrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b5) alkyl acrylamide/methacrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b6) alkyl acrylamide/methyl methacrylic acid/alkylaminoalkyl (meth)-acrylic acid copolymers,

b7) alkyl acrylamide/alkyl methacrylate/alkylaminoethyl methacrylate/ alkyl methacrylate copolymers,

b8) copolymers of

b8i) unsaturated carboxylic acids,

b8ii) cationically derivatized unsaturated carboxylic acids,

b8iii) optionally other ionic or nonionic monomers,

c) water-soluble zwitterionic polymers from the group of

c1) acrylamidoalkyl trialkylammonium chloride/acrylic acid copolymers and alkali metal and ammonium salts thereof,

c2) acrylamidoalkyl trialkylammonium chloride/methacrylic acid copolymers and alkali metal and ammonium salts thereof,

c3) methacroyl ethyl betaine/methacrylate copolymers,

d) water-soluble anionic polymers from the group of

d1) vinyl acetate/crotonic acid copolymers,

d2) vinyl pyrrolidone/vinyl acrylate copolymers,

d3) acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,

d4) graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or polyalkylene glycols,

d5) grafted and crosslinked copolymers from the copolymerization of

d5i) at least one monomer of the nonionic type,

d5ii) at least one monomer of the ionic type,

d5iii) polyethylene glycol and

d5iv) a crosslinking agent,

d6) copolymers obtained by copolymerization of at least one monomer of each of the following three groups:

d6i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,

d6ii) unsaturated carboxylic acids,

d6iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group d6ii) with saturated or unsaturated, linear or branched C_{8-18} alcohols,

d7) terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl ester,

d8) tetrapolymers and pentapolymers of

d8i) crotonic acid or allyloxyacetic acid,

d8ii) vinyl acetate or vinyl propionate,

d8iii) branched allyl or methallyl esters,

d8iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters,

d9) crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinyl benzene, vinyl methyl ether, acrylamide and water-soluble salts thereof,

d10) terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic monocarboxylic acid branched in the α-position,

e) water-soluble cationic polymers from the group of

e1) quaternized cellulose derivatives,

e2) polysiloxanes containing quaternary groups,

e3) cationic guar derivatives,

e4) polymeric dimethyl diallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid,

e5) copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate,

e6) vinyl pyrrolidone/methoimidazolinium chloride copolymers,

e7) quaternized polyvinyl alcohol,

e8) polymers known by the INCI names of polyquaternium 2, polyquaternium 17, polyquaternium 18 and polyquaternium 27.

This use of the above-mentioned polymers in accordance with the invention leads to coated tablets with advantageous properties, as the following Examples show. The foregoing observations on the process according to the invention apply equally to preferred embodiments of the use according to the invention (ingredients, composition of the premix, preferred polymers, etc.).

Examples

To produce uncoated detergent tablets, surfactant granules were mixed with other ingredients and tabletted in an eccentric tablet press. The composition of the surfactant granules is shown in Table 1 below while the composition of the premix to be tabletted (and hence the composition of the tablets) is shown in Table 2.

Table 1:

Surfactant granules [% by weight]

C_{9-13} alkyl benzenesulfonate	18.4
C_{12-18} fatty alcohol sulfate	4.9
C_{12-18} fatty alcohol · 7 EO	4.9
Soap	1.6
Sodium carbonate	18.8
Sodium silicate	5.5
Zeolite A (water-free active substance)	31.3
Optical brightener	0.3
Na hydroxyethane-1,1-diphosphonate	0.8
Acrylic acid/maleic acid copolymer	5.5
Water, salts	Balance

Table 2:

Premix [% by weight]

Surfactant granules	62.95
Sodium perborate monohydrate	17.00
Tetraacetyl ethylenediamine	7.30
Foam inhibitor	3.50
Enzymes	1.70
Repel-O-Tex® SRP 4*	1.10
Perfume	0.45
Zeolite A	1.00
Cellulose	5.00

** Terephthalic acid/ethylene glycol/polyethylene glycol ester (Rhodia, Rhône-Poulenc)

The tablettable premix was tabletted in a Korsch eccentric press (tablet diameter 44 mm, tablet height 22 mm, tablet weight 37.5 g).

The resulting tablets were divided up into three series, of which the first series was used untreated as Comparison Example C while the second series E1 was sprayed with a 20% by weight solution of a polyvinyl pyrrolidone/polyvinyl acetate copolymer in ethanol/water. The third series E2 was sprayed with a solution of polyvinyl pyrrolidone/vinyl alcohol copolymer and butyl aminoethyl methacrylate in water/isopropanol. In both cases E1 and E2, dimethyl ether was used as the propellent for the dispersions which were atomized to a droplet size of 30 µm. In the case of Example E1, 150 mg of the polymer was applied as the coating corresponding to a ratio of uncoated tablet to coating of 250:1. In Example E2 according to the invention, 100 mg of polymer were applied (corresponding to a ratio of uncoated tablet to coating of 375:1) and the test was repeated with only 50 mg of polymer (E2', corresponding to a ratio

of uncoated tablet to coating of 750:1).

Two tablets from each of the three series C, E1 and E2 were placed on a 4 mm mesh sieve and shaken for 120 seconds at maximum amplitude on a Retsch sieving machine. After this test, the weight loss of the tablets was determined. Table 3 below shows the weight loss of tablets E1, E2 and C, the values representing the average values of five determinations.

To determine tablet disintegration, a tablet was placed in a glass beaker filled with water (600 ml water, temperature 30°C) and the time taken for the tablet to disintegrate completely was measured. The experimental data of the individual tablet series are shown in Table 3:

Table 3:

Detergent tablets [physical data]

Tablet	**E1**	**E2**	**E2'**	**V**
Weight loss [% by weight]	3.36	4.0	4.3	6.7
Tablet disintegration [s]	15	14	13	13

The results show that abrasion can be distinctly reduced, even with extremely small amounts of coating material, without any effect on the disintegration time.

CLAIMS

1. Detergent tablets of compacted particulate detergent containing builder(s), surfactant(s) and optionally other detergent ingredients, characterized in that the tablets are coated with a polymer or polymer mixture, the polymer or at least 50% by weight of the polymer mixture being selected from

a) water-soluble nonionic polymers from the group of

a1) polyvinyl pyrrolidones,

a2) vinyl pyrrolidone/vinyl ester copolymers,

a3) cellulose ethers

b) water-soluble amphoteric polymers from the group of

b1) alkyl acrylamide/acrylic acid copolymers,

b2) alkyl acrylamide/methacrylic acid copolymers,

b3) alkyl acrylamide/methyl methacrylic acid copolymers,

b4) alkyl acrylamide/acrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b5) alkyl acrylamide/methacrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b6) alkyl acrylamide/methyl methacrylic acid/alkylaminoalkyl (meth)-acrylic acid copolymers,

b7) alkyl acrylamide/alkyl methacrylate/alkylaminoethyl methacrylate/ alkyl methacrylate copolymers,

b8) copolymers of

b8i) unsaturated carboxylic acids,

b8ii) cationically derivatized unsaturated carboxylic acids,

b8iii) optionally other ionic or nonionic monomers,

c) water-soluble zwitterionic polymers from the group of

c1) acrylamidoalkyl trialkylammonium chloride/acrylic acid copolymers and alkali metal and ammonium salts thereof,

c2) acrylamidoalkyl trialkylammonium chloride/methacrylic acid copolymers and alkali metal and ammonium salts thereof,

c3) methacroyl ethyl betaine/methacrylate copolymers,

d) water-soluble anionic polymers from the group of

d1) vinyl acetate/crotonic acid copolymers,

d2) vinyl pyrrolidone/vinyl acrylate copolymers,

d3) acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,

d4) graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or polyalkylene glycols,

d5) grafted and crosslinked copolymers from the copolymerization of

- d5i) at least one monomer of the nonionic type,
- d5ii) at least one monomer of the ionic type,
- d5iii) polyethylene glycol and
- d5iv) a crosslinking agent,

d6) copolymers obtained by copolymerization of at least one monomer of each of the following three groups:

- d6i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,
- d6ii) unsaturated carboxylic acids,
- d6iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group d6ii) with saturated or unsaturated, linear or branched C_{8-18} alcohols,

d7) terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl

ester,

d8) tetrapolymers and pentapolymers of

d8i) crotonic acid or allyloxyacetic acid,

d8ii) vinyl acetate or vinyl propionate,

d8iii) branched allyl or methallyl esters,

d8iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters,

d9) crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinyl benzene, vinyl methyl ether, acrylamide and water-soluble salts thereof,

d10) terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic monocarboxylic acid branched in the α-position,

e) water-soluble cationic polymers from the group of

e1) quaternized cellulose derivatives,

e2) polysiloxanes containing quaternary groups,

e3) *cationic guar derivatives*,

e4) polymeric dimethyl diallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid,

e5) copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate,

e6) vinyl pyrrolidone/methoimidazolinium chloride copolymers,

e7) quaternized polyvinyl alcohol,

e8) polymers known by the INCI names of polyquaternium 2, polyquaternium 17, polyquaternium 18 and polyquaternium 27.

2. Detergent tablets as claimed in claim 1, characterized in that the ratio by weight of uncoated tablet to coating is greater than 100:1, preferably greater than 250:1 and more preferably greater than 500:1.

3. Detergent tablets as claimed in claim 1 or 2, characterized in that the

thickness of the coating on the tablet is between 0.1 and 150 µm, preferably between 0.5 and 100 µm and more preferably between 5 and 50 µm.

4. Detergent tablets as claimed in any of claims 1 to 3, characterized in that, in addition to the polymers mentioned, the coating contains polyurethanes in quantities of 5 to 50% by weight, preferably in quantities of 7.5 to 40% by weight and more preferably in quantities of 10 to 30% by weight, based on the coating.

5. Detergent tablets as claimed in any of claims 1 to 4, characterized in that they additionally contain a disintegration aid, preferably a cellulose-based disintegration aid, preferably in granular, co-granulated or compacted form, in quantities of 0.5 to 10% by weight, preferably in quantities of 3 to 7% by weight and more preferably in quantities of 4 to 6% by weight, based on tablet weight, preferred disintegration aids having mean particle sizes above 300 µm, preferably above 400 µm and more preferably above 500 µm.

6. Detergent tablets as claimed in any of claims 1 to 5, characterized in that they contain anionic and/or nonionic surfactant(s) and have total surfactant contents above 2.5% by weight, preferably above 5% by weight and more preferably above 10% by weight, based on tablet weight.

7. A process for the production of coated detergent tablets by tabletting a particulate premix in known manner and dipping the resulting tablets in or spraying them with a melt, solution or dispersion of one or more polymers from the group of

a) water-soluble nonionic polymers from the group of

a1) polyvinyl pyrrolidones,

a2) vinyl pyrrolidone/vinyl ester copolymers,

a3) cellulose ethers

b) water-soluble amphoteric polymers from the group of

b1) alkyl acrylamide/acrylic acid copolymers,

b2) alkyl acrylamide/methacrylic acid copolymers,

b3) alkyl acrylamide/methyl methacrylic acid copolymers,

b4) alkyl acrylamide/acrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b5) alkyl acrylamide/methacrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b6) alkyl acrylamide/methyl methacrylic acid/alkylaminoalkyl (meth)-acrylic acid copolymers,

b7) alkyl acrylamide/alkyl methacrylate/alkylaminoethyl methacrylate/ alkyl methacrylate copolymers,

b8) copolymers of

  b8i) unsaturated carboxylic acids,

  b8ii) cationically derivatized unsaturated carboxylic acids,

  b8iii) optionally other ionic or nonionic monomers,

c) water-soluble zwitterionic polymers from the group of

c1) acrylamidoalkyl trialkylammonium chloride/acrylic acid copolymers and alkali metal and ammonium salts thereof,

c2) acrylamidoalkyl trialkylammonium chloride/methacrylic acid copolymers and alkali metal and ammonium salts thereof,

c3) methacroyl ethyl betaine/methacrylate copolymers,

d) water-soluble anionic polymers from the group of

d1) vinyl acetate/crotonic acid copolymers,

d2) vinyl pyrrolidone/vinyl acrylate copolymers,

d3) acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,

d4) graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or

polyalkylene glycols,

d5) grafted and crosslinked copolymers from the copolymerization of

d5i) at least one monomer of the nonionic type,

d5ii) at least one monomer of the ionic type,

d5iii) polyethylene glycol and

d5iv) a crosslinking agent,

d6) copolymers obtained by copolymerization of at least one monomer of each of the following three groups:

d6i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,

d6ii) unsaturated carboxylic acids,

d6iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group d6ii) with saturated or unsaturated, linear or branched C_{8-18} alcohols,

d7) terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl ester,

d8) tetrapolymers and pentapolymers of

d8i) crotonic acid or allyloxyacetic acid,

d8ii) vinyl acetate or vinyl propionate,

d8iii) branched allyl or methallyl esters,

d8iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters,

d9) crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinyl benzene, vinyl methyl ether, acrylamide and water-soluble salts thereof,

d10) terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic monocarboxylic acid branched in the α-position,

e) water-soluble cationic polymers from the group of

e1) quaternized cellulose derivatives,

e2) polysiloxanes containing quaternary groups,

e3) cationic guar derivatives,

e4) polymeric dimethyl diallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid,

e5) copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate,

e6) vinyl pyrrolidone/methoimidazolinium chloride copolymers,

e7) quaternized polyvinyl alcohol,

e8) polymers known by the INCI names of polyquaternium 2, polyquaternium 17, polyquaternium 18 and polyquaternium 27.

8. A process as claimed in claim 7, characterized in that an aqueous solution of one or more polymers from groups a) to e) is sprayed onto the tablets, the aqueous solution containing, based on the solution, 1 to 20% by weight, preferably 2 to 15% by weight and more preferably 4 to 10% by weight of polymer(s) from groups a) to e), optionally up to 20% by weight, preferably up to 10% by weight and more preferably below 5% by weight of one or more water-miscible solvents and - for the rest - water.

9. A process as claimed in claim 7 or 8, characterized in that an aqueous dispersion of one or more polyurethanes additionally containing one or more dissolved polymers from groups a) to e) is sprayed onto the tablets, the dispersion containing, based on the dispersion, 1 to 20% by weight, preferably 2 to 15% by weight and more preferably 4 to 10% by weight of polyurethane(s), 1 to 20% by weight, preferably 2 to 15% by weight and more preferably 4 to 10% by weight of polymer(s) from groups a) to e), optionally up to 20% by weight, preferably up to 10% by weight and more preferably below 5% by weight of one or more water-miscible solvents and - for the rest - water.

10. A process as claimed in claim 7, characterized in that a solution or dispersion of one or more polymers from groups a) to e) in a solvent or solvent mixture from the group consisting of water, ethanol, propanol, isopropanol, n-heptane and mixtures thereof is sprayed onto the tablets using inert propellents from the group consisting of nitrogen, dinitrogen oxide, propane, butane, dimethyl ether and mixtures thereof.

11. A process as claimed in claim 10, characterized in that the solution or dispersion has the following composition:

iv) 30 to 99% by weight, preferably 40 to 90% by weight and more preferably 50 to 85% by weight of ethanol, propanol, isopropanol, n-heptane or mixtures thereof,

v) 0 to 20% by weight, preferably 1 to 15% by weight and more preferably 2 to 10% by weight of water,

vi) 1 to 50% by weight, preferably 2 to 25% by weight and more preferably 3 to 10% by weight of one or more polymers from groups a) to e).

12. A process as claimed in any of claims 7 to 11, characterized in that the particular solution and/or dispersion is sprayed onto the tablets through a nozzle, the average droplet size in the spray mist being less than 100 µm, preferably less than 50 µm and more preferably less than 35 µm.

13. A process as claimed in any of claims 7 to 12, characterized in that the tablet to be coated is obtained by tabletting a particulate premix which contains surfactant-containing granule(s) and has a bulk density of at least 500 g/l, preferably at least 600 g/l and more preferably at least 700 g/l.

14. A process as claimed in claim 13, characterized in that the surfactant-containing granules have particle sizes between 100 and 2000 µm, preferably between 200 and 1800 µm, more preferably between 400 and 1600 µm and most preferably between 600 and 1400 µm.

15. A process as claimed in claim 13 or 14, characterized in that the surfactant-containing granules contain anionic and/or nonionic surfactants and builders and have total surfactant contents of at least 10% by weight,

preferably at least 20% by weight and more preferably at least 25% by weight.

16. A process as claimed in any of claims 13 to 15, characterized in that the particulate premix additionally contains one or more substances from the group of bleaching agents, bleach activators, disintegration aids, enzymes, pH regulators, perfumes, perfume carriers, fluorescers, dyes, foam inhibitors, silicone oils, redeposition inhibitors, optical brighteners, discoloration inhibitors, dye transfer inhibitors and corrosion inhibitors.

17. The use of polymers or polymer mixtures for coating detergent tablets, the polymer or at least 50% by weight of the polymer mixture being selected from

a) water-soluble nonionic polymers from the group of

a1) polyvinyl pyrrolidones,

a2) vinyl pyrrolidone/vinyl ester copolymers,

a3) cellulose ethers

b) water-soluble amphoteric polymers from the group of

b1) alkyl acrylamide/acrylic acid copolymers,

b2) alkyl acrylamide/methacrylic acid copolymers,

b3) alkyl acrylamide/methyl methacrylic acid copolymers,

b4) alkyl acrylamide/acrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b5) alkyl acrylamide/methacrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b6) alkyl acrylamide/methyl methacrylic acid/alkylaminoalkyl (meth)-acrylic acid copolymers,

b7) alkyl acrylamide/alkyl methacrylate/alkylaminoethyl methacrylate/alkyl methacrylate copolymers,

b8) copolymers of

b8i) unsaturated carboxylic acids,

b8ii) cationically derivatized unsaturated carboxylic acids,

b8iii) optionally other ionic or nonionic monomers,

c) water-soluble zwitterionic polymers from the group of

c1) acrylamidoalkyl trialkylammonium chloride/acrylic acid copolymers and alkali metal and ammonium salts thereof,

c2) acrylamidoalkyl trialkylammonium chloride/methacrylic acid copolymers and alkali metal and ammonium salts thereof,

c3) methacroyl ethyl betaine/methacrylate copolymers,

d) water-soluble anionic polymers from the group of

d1) vinyl acetate/crotonic acid copolymers,

d2) vinyl pyrrolidone/vinyl acrylate copolymers,

d3) acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,

d4) graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or polyalkylene glycols,

d5) grafted and crosslinked copolymers from the copolymerization of

d5i) at least one monomer of the nonionic type,

d5ii) at least one monomer of the ionic type,

d5iii) polyethylene glycol and

d5iv) a crosslinking agent,

d6) copolymers obtained by copolymerization of at least one monomer of each of the following three groups:

d6i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,

d6ii) unsaturated carboxylic acids,

d6iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group d6ii) with saturated or unsaturated, linear or branched C_{8-18} alcohols,

d7) terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl ester,

d8) tetrapolymers and pentapolymers of

d8i) crotonic acid or allyloxyacetic acid,

d8ii) vinyl acetate or vinyl propionate,

d8iii) branched allyl or methallyl esters,

d8iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters,

d9) crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinyl benzene, vinyl methyl ether, acrylamide and water-soluble salts thereof,

d10) terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic monocarboxylic acid branched in the α-position,

e) water-soluble cationic polymers from the group of

e1) quaternized cellulose derivatives,

e2) polysiloxanes containing quaternary groups,

e3) cationic guar derivatives,

e4) polymeric dimethyl diallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid,

e5) copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate,

e6) vinyl pyrrolidone/methoimidazolinium chloride copolymers,

e7) quaternized polyvinyl alcohol,

e8) polymers known by the INCI names of polyquaternium 2, polyquaternium 17, polyquaternium 18 and polyquaternium 27.

Abstract

Coated detergent tablets with advantageous properties, such as high hardnesses but short disintegration times and high resistance to impact and friction, are obtained with relatively small amounts of coating materials, at most 1% by weight - preferably far less - of the tablet as a whole being made up by the coating material. Suitable coating materials are selected water-soluble polymers which may also be used in the form of mixtures with other polymers.